ENVIRONMENTAL RESEARCH

PROSPECTS FOR THE UTILIZATION OF PAPER MILL SLUDGES IN MANUFACTURED PRODUCTS

RAC Project No. 721C
FINAL REPORT

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FINAL REPORT

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EXECUTIVE SUMMARY

On behalf of the Ontario Ministry of the Environment and Energy, ORTECH completed a technical review of available literature to define the prospects of using paper industry sludges in commercial product applications. This report summarizes the results of the review.

The significance of paper sludge management is due to the large quantities involved, and expected increases in output due to expanding deinking capacity, and improvements to effluent treatment plants. Current landfill disposal practices are undesirable from regulatory and economic perspectives. Incineration is viable for high-fibre primary sludges. In contrast, high-ash sludges from fine papers and deinking operations could result in high operating and maintenance costs. Land application represents a cost-effective and beneficial sludge use option. However, land application of paper sludges has not been widely adopted.

The physical, chemical and biological properties of paper industry sludges are determined by manufacturing and effluent treatment processes. Among the integrated pulp and paper mills in Ontario, various processes are employed for pulpwood debarking, wood preparation, pulping and paper making. The major pulping processes employed include: mechanical - groundwood, thermomechanical; chemical - kraft, sulfite, semichemical; recycled - paperboard, deinking. There is considerable overlap among the various paper products relative to pulping processes. Moreover, many mills employ combinations of different processes, e.g. groundwood and kraft or thermomechanical and deinking, for a variety of papers. Due to the varying configurations of mill processes and product lines, effluent characteristics, and, hence, sludge properties will vary on a mill-by-mill basis.

Paper industry sludges from primary effluent treatment contain cellulosic fibre and clay fillers/coatings which have potential value for recycling back into paper making operations, or use in other manufactured product and commercial applications. Secondary effluent treatment processes are being added to a number of mills, especially at northern locations. Secondary treatment sludges are rich in organic matter, primarily as wasted biomass and associated colloidal matter. These materials are usually combined with primary sludges for dewatering, and land disposal.

Sludges from newsprint, and paperboard operations tend to be rich in cellulosic matter, while sludges from fine papers, bond and ledger stock, for example, contain substantial amounts of ash, primarily clay fillers and coatings. High ash sludges also result from deinking operations due to the removal of clay fillers and coatings during repulping processes. Organic matter in combined primary and secondary sludges will consist of fibrous and non-fibrous matter. Available data show that deinking operations generate substantially greater quantities of sludge relative to virgin fibre operations. Also, the physical and chemical composition of deinked secondary fibre sludges is more variable. The properties of paper industry sludges could have a significant impact on the quality and performance of manufactured products.

Potential uses for paper sludges were grouped into two categories, as follows:

(1) material recovery and recycling
(2) manufactured products and commercial applications.

Substantial research has examined the direct recycling of primary and some combined primary and secondary sludges back into the paper making process, especially for paper board. Also, since the early 1950s, various strategies and technologies, such as calcination, wet air oxidation and screening, have been examined for the recovery of usable long fibre and filler materials for paper making. High fibre sludges are amenable to fibre recovery, while high ash sludges from fine papers are suitable for the recovery of fibre and fillers. At least one U.S. mill, Prime Fibre Inc., has developed commercial operations for the production of market pulp and filler substitutes from paper sludges.

Among the manufactured product applications, sludge uses in cementitious composites, cement and fibre composites have received considerable attention, and are attractive. In these cases, whole sludges can be utilized with minimal processing, and experimental results have shown acceptable product qualities. The principal constraints to using sludges in these applications are associated with mill proximity to manufacturing plants, and, hence, handling costs, mill location and market availability. From a technical perspective, the major issue is that cementitious composites containing paper sludges have not been subjected to long-term stability and performance testing.

Other sludge uses in fermentation products (e.g. ethanol, protein recovery) have been examined under laboratory conditions. Substantial developmental work would be required to define the technical and practical feasibility of these applications for paper sludges, and especially for combined primary and secondary sludge materials. At least one pulp and paper company established a commercial livestock feed operation based on secondary sludge. This operation was suspended due to poor markets and product palatability.

Market issues have been a major impediment to using paper industry sludges in manufactured products. Location of individual mills, local manufacturing capacity and product lines need to be assessed relative to product markets. It is also clear that sample products, product performance and formulations need to be more extensively assessed to satisfy manufacturers and markets.

Due to the growth of green industries, and programs such as Build Green, market prospects and opportunities could be improved.

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1. INTRODUCTION

In 1994, the Ontario Ministry of the Environment and Energy (MOEE) awarded two research contracts on potential uses of paper industry sludges in manufactured product and commercial applications. ORTECH was awarded one contract to complete a technical review of available literature, to establish the state-of-the-art relative to mill sludge management options, and to identify, where possible, prospects for commercial development. The second project, awarded to the University of Toronto under the direction of Dr. Honghi Tran, examined general and specific sludge applications in cementitious materials.

This report provides a summary of the technical review and related information on the broad spectrum of paper industry sludge uses in manufactured products from available technical literature. It is an adjunct to the more detailed work undertaken by Dr. H. Tran and colleagues, on cementitious materials.

The initial search for technical information identified a substantial body of literature on various mill sludge applications other than landfill disposal, incineration and land application. Due to the volume of literature, and limited access to documents from off-shore sources, it is difficult to provide a comprehensive review of each technology, at this time. Sufficient information was obtained to provide descriptions and assessments of sludge use alternatives. Where possible, original citations and other reference materials have been identified for more focussed analysis of individual technologies.

2. OBJECTIVES AND GOALS

ORTECH proposed a two phased project, the first phase of which was dedicated to a technical review of available information on paper industry sludge use. The second phase was defined to address specific applications, product development and testing. The content of this report is limited to Phase 1. Phase 1 objectives and goals can be summarized as follows:

(a) Technical review of manufactured product applications for paper industry sludges from available literature

(b) Identify manufacturing and treatment processes which define the composition of mill sludges

(c) Define the compositional attributes of sludges which could affect their utilization

(d) Identify general and specific sludge applications which have potential for commercialization

(e) Preliminary assessment of economic, market and other factors which have affected sludge use.

3. INFORMATION RESOURCES

The principal sources of information used in this report were available technical reports, peer reviewed papers, trade journal papers and patents. Direct contact with company or mill representatives produced minimal information beyond that currently in the public domain. Due to the sensitivity of sludge management at the individual mill and industry-wide levels, disclosure was limited.

An on-line search of available databases was initiated in June, 1994, to capture all documents relevant to pulp and paper sludge management and use. A total of 268 references was identified. Titles and accompanying abstracts were screened to eliminate documents associated with landfill related technologies and applications or sludge incineration technologies.

Acquisition of available documents was the most difficult task. Technical reports, papers and patents from North American sources were the easiest to obtain. However, complete and comprehensive collections of documents are lacking at individual institutions. Private collections associated with corporate research facilities or industry agencies could not be accessed through inter-library loan networks outside Canada. Industry sponsored projects and reports completed before 1980 may be out of print, and thus, tracking sources of original documents is difficult. Costs for acquiring individual documents varied from $8.00 for short papers to $40.00 or more for larger technical reports. Individuals or companies not affiliated with forest industry agencies or associations may have considerable difficulty in accessing these resources.

It was evident from the search that a substantial body of technical literature originated from off-shore sources. Due to the general lack of North American holdings, it is necessary to obtain these documents directly from sources in the respective countries. References can be obtained from Britain, Germany, France, and Scandinavian countries with relative ease. Incomplete citations and obscure sources in Poland, Bulgaria, Rumania and Russia, for example, prevented acquisitions. The listing of reports and patents originating in Japan is impressive; however, North American sources were not readily identified. The costs associated with the search, acquisition and translation of offshore documents for this protect were prohibitive. Moreover, the time frame for document acquisitions from these sources was indeterminate. Thus, much of the information in this report is biased towards North American experience, although secondary citations have been utilized, where possible, to fill gaps relative to foreign technologies. The technical content of this report is based primarily on approximately 100 technical documents from internal and external sources.

4. PROBLEM STATEMENT

The significance of pulp and paper mill sludge management as a contemporary environmental issue is recognized both from industry and regulatory perspectives. Two workshops held in 1994 underscore this point. In February, 1994, a one day workshop, held at the University of Toronto, and sponsored by the MOEE, brought together representatives from the pulp and paper industry in Ontario, Provincial and Federal agencies, and scientists and engineers to specifically address the issue of paper industry sludge management. The second event, held in Ottawa in March, 1994, addressed the general environmental issues affecting the industry at a national level. The outcome of this workshop was published to highlight the major issues and resolutions (Industry Canada, 1994). Of the solid waste management issues facing the pulp and paper industry, sludge disposal or management was identified as being the most significant.

Why is sludge management a significant issue? The simplest response to this question is that the quantities of sludge generated by the pulp and paper industry are substantial. In Ontario alone, it is estimated that approximately 500,000 dry T, or 1.4 MT wet weight at 35% total solids, of paper industry sludge are generated annually. This estimate is based on typical material losses and wastage from the various pulp and paper manufacturing systems. For instance, Bruce (1994) noted that combined primary and secondary sludge output (dry weight basis) from kraft, groundwood and deinking operations amounted to 33, 50 and 160-300 Kg/air dry T of product, respectively. For deinking operations, the lower sludge outputs are associated with newsprint, while the highest levels are associated with the processing of ledger, and uncoated book stock. On a wet weight basis, the sludge output from deinking plants may approximate the total paper production capacity, in some cases (Bruce, 1994).

Wet weight estimates of sludge output are based on an average 35% total solids content in dewatered sludge, and approximate the quantities sent to disposal. Data in-hand for a variety of mills have indicated the following wet sludge generation rates: 20 T/day (primary only) from non-integrated fine and specialty paper mills; about 60 T/day (primary only) from integrated sulfite-groundwood-deinking operations; 60 T/day (primary only) from a deinking-tissue mill; 300 T/day from deinked (100%) tissue-newsprint production; and; 200 T/day from deinked (70%) newsprint-thermomechanical-groundwood operations. Unsubstantiated forecasts suggest that sludge output will double by the year 2,000 based on recent trends relative to deinking processes and additional effluent treatment capabilities.

4.1 Deinking as a Sludge Source

Although paper fibre recycling and deinking operations have been around since the beginning of the pulp and paper industry in Canada (Howard, 1994), market demands and legislation since the late 1980s has resulted in expanding capacity for the deinking and utilization of secondary fibre. As indicated by Sittig (1977) between 1949 and 1969 secondary fibre utilization accounted for 20-21% of the total fibre used. Smook (1982) showed that secondary fibre use in the U.S. increased to around 25% by the early 1980s. Most of the paper produced in Canada is exported, with the U.S. representing the major market, based on Lockwood-Post's (1994) industry statistics. Domestic sources of waste paper are inadequate to meet both domestic and export requirements for recycle content paper, and, thus, it has been necessary to import waste paper. The quantities of waste paper imported to Canada (CPPA, 1994) have increased as shown in Figure 1, and, indirectly, highlight trends relative to waste paper utilization and deinking. Also shown in Figure 1 are the quantities of waste paper recovery from domestic sources.

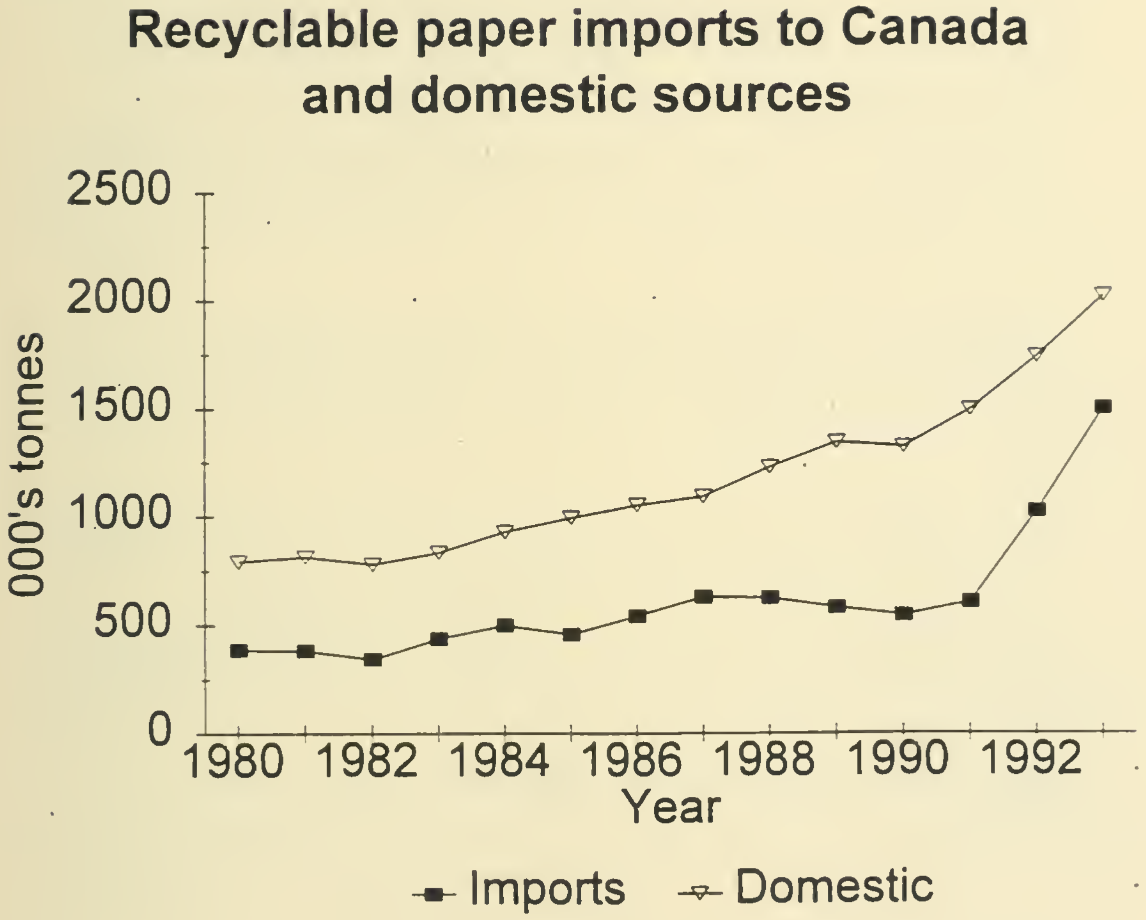


Figure 1: Waste paper imports to Canada from the U.S. and off-shore sources, plus domestic sources. Imports of waste paper have increased from 34.1% to 42.5% of consumption. Source: CPPA (1994)

The linkage between deinking activity and higher sludge output is associated with high losses of small fibres and the removal of clay fillers, coatings, inks and other solids relative to similar losses encountered with virgin fibre processing (Sittig, 1977). As indicated above, the quantities of sludge generated by deinking operations are substantially higher than those associated with virgin fibre processes such as kraft, sulfite, and mechanical pulp and paper production. Due to the need to import waste paper to fulfil market demands, a waste management problem associated with sludges is also imported.

The demand for recycle content paper is high, and has resulted in the need to process poor quality waste paper, a factor which could lead to higher waste generation.

The emphasis in paper recycling has been the achievement of high quality secondary fibre based products (Howard, 1994). It has been acknowledged that waste generation rates from deinking plants are high, and that future efforts will become focussed on process optimization, and the adoption of strategies to improve fibre recovery, and the reclamation of usable fillers. Current shortages of waste paper have resulted in processing of low grade materials, and may lead to improvements in the recovery of usable fibre from waste paper and sludges in the near future.

As discussed subsequently, efforts to recover fibre and fillers from waste paper and sludges have been examined since the early 1950s. Recent research has shown that fibre and filler reclamation is achievable (Maxham, 1992b). Howard (1994) suggested that process optimization may also lead to the retention of fillers on the front-end of recycling and deinking operations. It is evident that improved fibre and filler recovery processes could reduce mill sludge output by >50% (Maxham, 1992b).

4.2 Effluent Treatment Plant Improvements

The second factor affecting the output of paper industry sludges involves improvements to existing effluent treatment plants. Stringent regulatory limits have been defined for the quality of effluents discharged by pulp and paper mills. Achieving these regulatory objectives requires the addition of secondary treatment capabilities at many Ontario mills, and may also require improvements to existing primary treatment systems. Most mills in Ontario possess some form of effluent treatment; few, however, rely on combined primary and secondary systems. The addition of secondary treatment capabilities could increase total sludge output by a factor of 1.3-2.0 at individual mills, due to the wasting of biomass, associated colloids and other fine solid materials. Secondary treatment systems are currently being added at a number of mills in Ontario with more to come before the end of 1996.

Interestingly, the majority of the treatment plant upgrades, including secondary treatment system additions, will occur at northern mills. In most cases, secondary treatment systems at pulp and paper mills are combined with primary treatment, simply because secondary treatment processes cannot accommodate, or treat, effluents containing high suspended solids contents (Sittig, 1977). As noted subsequently, the conventional practice has been to combine primary and secondary mill sludges before dewatering to eliminate the problems associated with the dewatering of wasted biomass.

A number of northern mills currently incinerate primary sludges with hog fuel as an energy supplement. Due to anticipated problems with dewatering secondary sludges, it may be necessary to divert primary sludges from incineration processes, which would require a fuel replacement, and, hence, increased operating costs. To avoid additional costs, due to the diversion of primary sludges, it may be necessary to develop or adopt separate strategies for the management of secondary sludges alone.

Representatives from two northern mills indicated that the management of secondary sludges was the most significant issue, based on the anticipated quantities involved (up to 50% of total sludge output), problems of handling, and economic consequences of diverting primary sludge and/or other combustible materials from incineration processes, for secondary sludge handling (ORTECH, 1993, Confid. sources).

4.3 Process Closure

Significant areas of active research and development by the industry include mill process closure. Process closure involves closed-cycle operations which minimize effluent (air, water, solid waste) discharges, and maximize the in-plant recycling of process waters and materials. The chemi-mechanical mill at Meadow Lake, Saskatchewan, was designed and built as a closed system operation, and, thus far, it has been a success. Towers and Wearing (1994) cited other examples from Europe, the U.S. and South Africa where closed system mill operations have been established. Although there are potential problems associated with the closure of chemical and mechanical pulp and paper mill operations due to excess heat, chemical accumulation and corrosion, among others, active research programs have been addressing the potential solutions (NCASI, 1976, 1978, 1980, 1982, 1988, 1993). The fact that closure has been achieved at mechanical, sulfite and some kraft mills would suggest that such operations could become more widespread in the foreseeable future. It is prudent to note that paperboard mills have already established a high degree of process closure, and at least one mill in Ontario achieved complete closure in late 1994.

Process closure on an industry wide or mill-by-mill basis would minimize effluent and waste output, thereby severely reducing the quantities of waste and sludge that could be used in manufactured products. The implications are significant with respect to the planning and development of manufacturing facilities that would use paper industry sludges. Gradual or rapid changes in mill processes towards system closure would limit the intermediate or long-term viability of sludge-based manufacturing operations. Moreover, such trends would likely discourage initial capital investment in manufacturing operations, near existing or new mills, if process closure is a goal.

4.4 Market Issues

Although the total paper sludge generation rate on a Province-wide basis underscores the extent of the problem in general, any options or alternatives for the use of these residuals must consider individual mill situations. The majority of non-integrated paper mills generate relatively small quantities of sludge (e.g. <20-40 T/day, wet weight basis) and are situated in urban areas where diverse commercial and industrial activities could probably assimilate sludges in various products. Most of the large integrated pulp and paper operations are situated in northern and remote locations, where local opportunities and prospects for using large quantities of sludge (e.g. 100 T/day or more) in commercial products are limited. High value added products or uses for sludge would be required to offset the costs of handling and transportation to larger market areas, such as southern Ontario or the U.S. Remote northern mill operations could, as a consequence, be shut out of commercial opportunities.

The vast majority of the alternative uses for paper industry sludges, including material recovery and recycling for paper making, described and discussed subsequently in this report, has been focussed on cellulosic fibre and/or fillers. Some processes or applications can accommodate combined primary and secondary sludges, and a number of claims from eastern European sources suggest that secondary sludge can be successfully used in paper making and other uses (Chernousev, 1983; Bukhteev et al, 1984; Ignatov and Evelevich, 1988). Substantial research is required to verify these results, since North American based experience has identified problems due to odours and poor product quality, with the use of secondary biological solids in paperboard processes (Rosenqvist, 1978; NCASI, 1979; McAndrew, 1985; Rundell, 1985). There are no explicitly defined operations in North America which recycle secondary sludge components in paper making.

4.5 Sludge Management Practices

Landfill disposal of paper industry sludges has been the most common management practice. Escalating landfill costs and regulatory policy discourage this option. A number of mills incinerate primary sludge with bark and wood wastes primarily as an economical fuel source. These practices may continue for some time due to the costs of replacement fuels. Although regulatory policy in Ontario allows pulp and paper industry sludge incineration, economic factors associated with emission controls (Pridham and Cline, 1988), and operating and maintenance problems (slagging and clinker formation) have discouraged this option (Bruce, 1994). High-ash content sludges from deinking and fine paper operations possess low fuel values and require supplements for combustion. As an example, trials using a deinked tissue sludge containing approximately 50% ash (dry weight basis) had a calorific value of 1,500 BTU/lb wet, and 3,500 BTU/lb dry. This particular material would not burn in the absence of an alternative fuel (ORTECH, 1990, confid. client). Direct land application of mill sludges can be beneficial to plant growth and soil conditioning, and is also cost-effective (NCASI, 1984; Thacker, 1986). A highly successful land application program was implemented in the Niagara region of Ontario in the early 1980s (Pridham and Cline, 1988).

The growth responses and performance of horticultural crops to paper sludge amended soil have been positive (Cline and Chong, 1991). Monitoring of soil and groundwater quality at specific sites has shown no adverse effects of consecutive annual applications of paper sludge (Bellamy et al, 1990; Bellamy and Parish, 1992). However, land application has not been widely accepted.

Since the 1940s at least, the pulp and paper industry has examined, and where possible, adopted various strategies for waste reduction (NCASI, 1993; Wiegand and Unwin, 1994). These efforts have included in-plant loss reduction, process water recycling and recycling of wastes and sludges in paper making processes. Considerable attention has been paid to utilization of sludges in various commercial applications such as: concrete and other cementitious materials, ceramics, composites, livestock feed, biofuels and fermentation products, and agricultural products, including biodegradable plant pots (Rosenqvist, 1978; Bianchin, 1981; Shimono, 1981; Harkin, 1982; Rogers, 1982; Valette, 1982; Przybysz, 1986; Pridham and Cline, 1988; Hamilton et al, 1991; NCASI, 1993). In spite of the research and development completed thus far, few of the alternative uses for paper industry sludges have achieved commercial scale success. The most recent data on paper sludge management practices in the U.S. were compiled by NCASI in 1989 (NCASI, 1992), and are summarized in Figure 2. Not shown in the diagram is the percentage of sludge used in manufactured product applications, which accounted for <1% of the sludge generated nationally. No similar data have been consolidated for Canadian mills, although a survey is currently in progress with Environment Canada support.

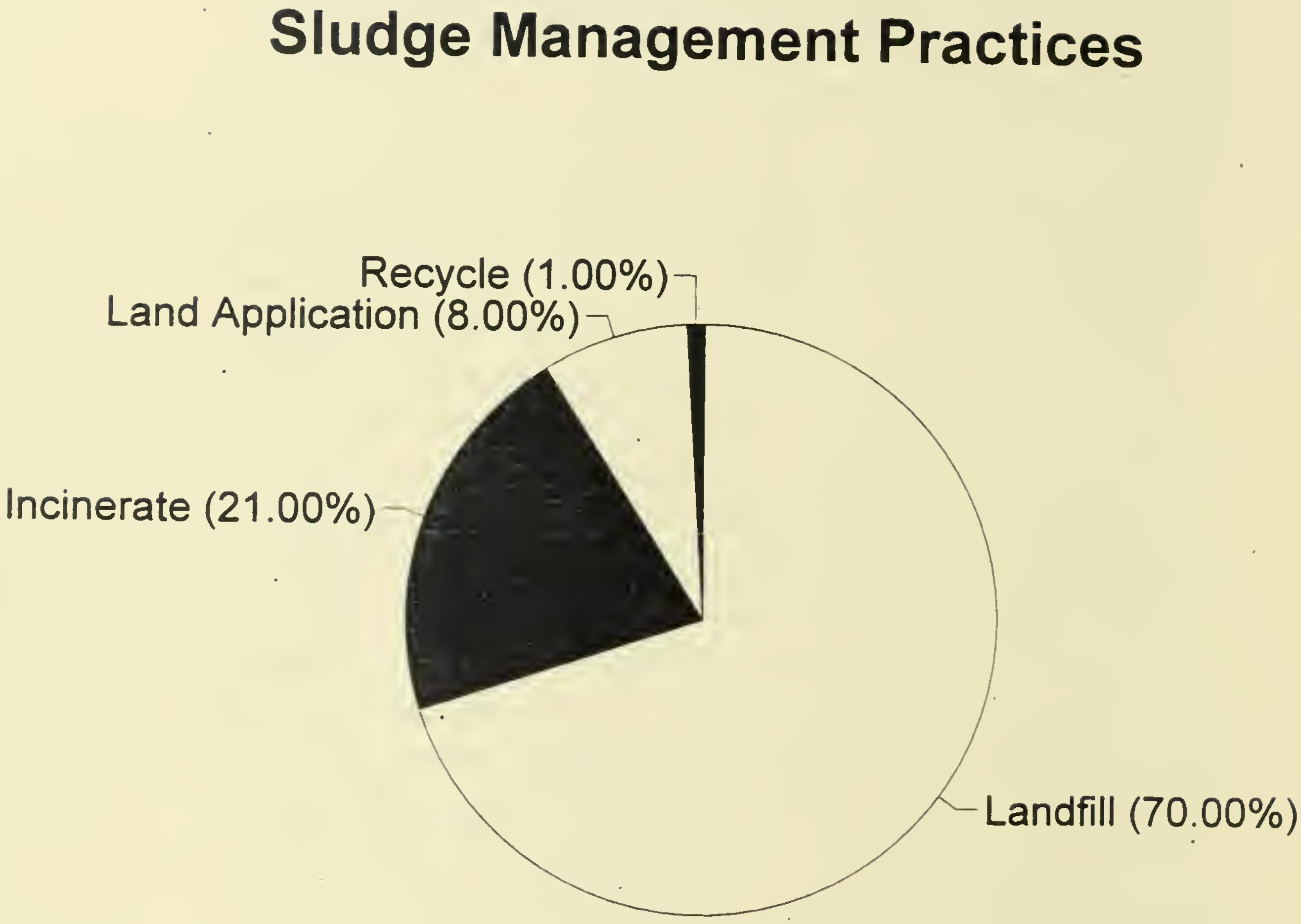


Figure 2: Paper industry sludge management practices in the U.S. based on a 1989 mill survey (NCASI, 1992). This represents the most recent survey data.

The lack of commercial scale uses for paper industry sludges has been attributed to a number of factors. First, many of the potential sludge uses were conceived before waste disposal was an issue, and when landfill disposal represented the most cost-effective option (NCASI, 1993; Wiegand and Unwin, 1994). Second, Harkin (1982), among others, has noted that variable and inconsistent compositional properties of paper industry sludges discouraged usage. The lack of manufacturing capabilities and capacity, adverse economics and limited or undefined market prospects have also been cited as reasons for the lack of commercial sludge uses.

Various recycling and 3Rs initiatives have, since the late 1980s, stimulated the growth of "green industries" which can utilize a variety of waste materials in new products. These developments have created opportunities, manufacturing capabilities and markets for commercial products containing wastes, which could include paper industry sludges. Due to these recent advancements, it is prudent to re-examine and, where possible, define prospects for the use of paper sludges in manufactured product applications.

5. INDUSTRY PROFILE

The physical, chemical and biological properties of paper industry sludges are determined by manufacturing processes and effluent treatment processes employed at individual mills. A basic understanding of manufacturing and effluent treatment processes is deemed to be necessary for defining prospects for sludge uses. In this regard, product formulations and performance could be highly influenced by the chemical and physical properties of the sludge, and must, therefore, be examined on a mill-by-mill basis. An overview of paper production and effluent treatment processes is presented in the following sections.

5.1 Product Groups, Pulping Categories and Mill Type

The American Paper Institute (API) classification identified six product groups and five pulping process categories. The general classification, adapted from Sittig (1977) is summarized in Table 1. There is considerable overlap among the product groups and pulping processes. For instance, kraft, sulfite and mechanical pulps are used in the manufacture of newsprint, various writing papers and packaging products. The recycled paper product group could include paperboard and deinked paper fibre materials which are derived from different repulping and manufacturing processes.

Paper product types vary in composition, which will have a significant impact on the compositional properties of effluent treatment plant sludges. In this regard, paper products, such as corrugating medium, paper board and newsprint are dominated by cellulosic fibre and contain relatively small quantities of inorganic fillers. Hence, sludges from these types of mills tend to be dominated by cellulosic solids. In contrast, clays and other inorganic materials (titanium dioxide, calcium carbonate, talc) are added to

TABLE 1: Pulp and paper product groups and process categories (American Paper Institute - Sittig, 1977).

A: Product Groups	
(A) Newsprint	
(B) Printing, writing and related types	Uncoated groundwood Machine/off-machine coated Book uncoated, chemical writing Cotton fibre Thin paper Solid bleached bristol
(C) Packing and industrial converting	Unbleached kraft Other packaging and converting Special industrial
(D) Tissue	
(E) Construction grades	
(F) Paperboard	Unbleached kraft Solid bleached packaging Semichemical paperboard Recycled

B: Process Categories	
(A) Dissolving	Sulfite sulfate (kraft)
(B) Sulfite	Softwood bleached Hardwood bleached Unbleached
(C) Sulfate (kraft)/soda	Softwood bleached Hardwood bleached Unbleached
(D) Semichemical	Bleached Unbleached
(E) Groundwood	

various writing and fine paper products. Sludges from fine paper production may contain 40-60% ash due to the fillers and coatings used. High, and often variable, ash contents are also encountered in sludges from deinking operations.

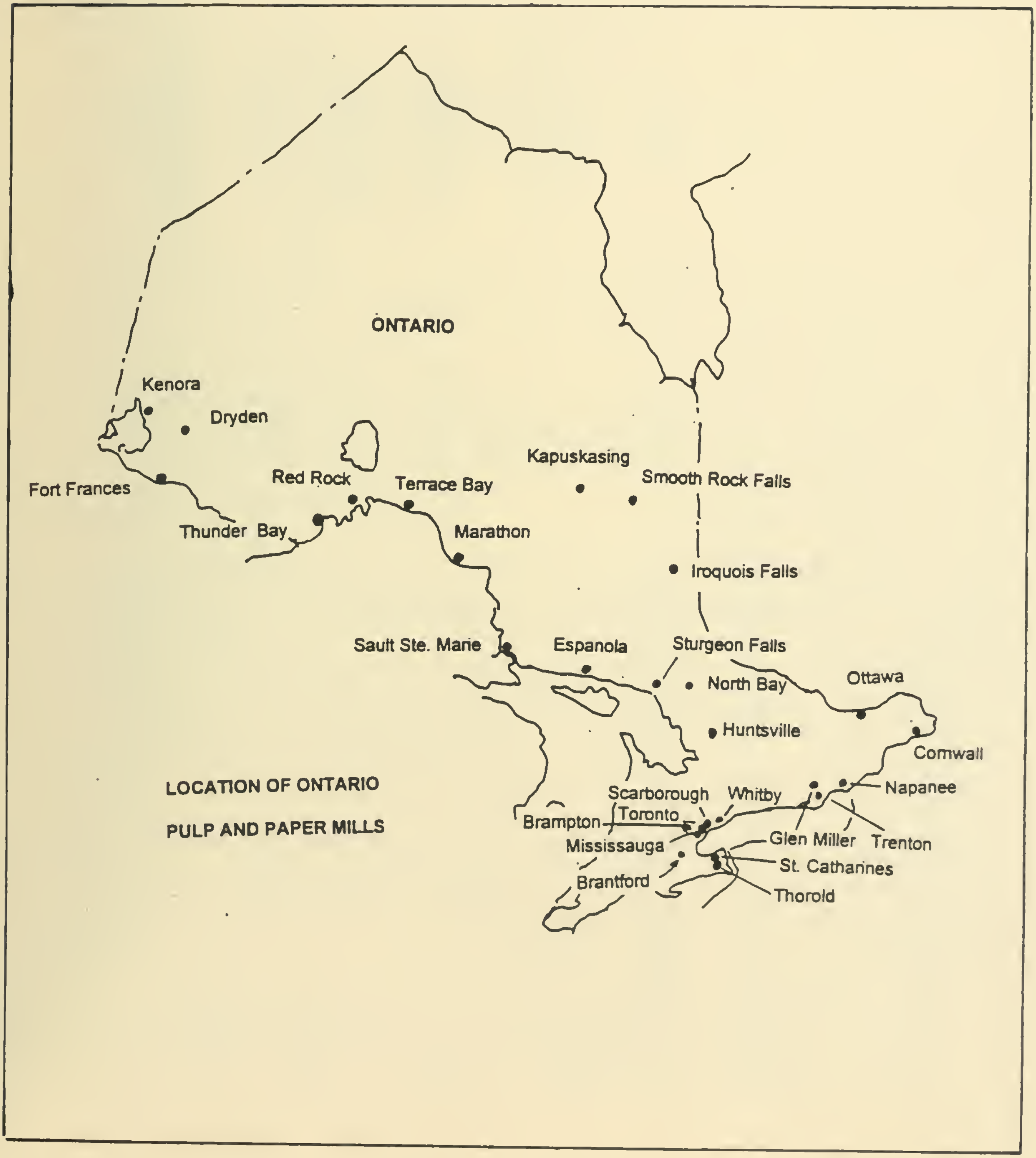
Mill types can generally be grouped into two categories - integrated pulp and paper mills, and non-integrated paper mills. Pulp mills could form a third category. Integrated pulp and paper mills produce pulp by one or more processes identified in Table 1, for on-site paper making, and may also produce market pulp for off-site use. Non-integrated paper mills are smaller in scale than integrated mills, and manufacture paper from market pulps. The category of pulp mills was added primarily to highlight operations which produce market pulp only. In this regard, three mills in Ontario produce market pulp only.

Deinking mills generally fall within the integrated pulp and paper mill category. In the U.S., there are a number of mills which produce market pulps only from deinked secondary fibre. Currently, no such operations exist in Ontario.

5.2 Ontario Mills

The Pulp and Paper Canada (1992) and Lockwood-Post (1994) directories list 36 pulp and paper mills in Ontario, one of which is indefinitely idle. The geographic distribution of Ontario mills is shown in Figure 3. Table 2 provides a summary of mill location, type, production lines, and capacity and effluent treatment systems. The majority of the mills in Ontario falls within the integrated pulp and paper mill category. The types of pulping processes employed at individual mills in Ontario vary from single processes (e.g. kraft, sulfite, semichemical) to combinations such as kraft-groundwood, sulfite-groundwood and sulfite-groundwood-deinking, for

Figure 3



LOCATION OF ONTARIO PULP AND PAPER MILLS

TABLE 2: ONTARIO MILL PRODUCT AND PULP CATEGORIES

The classifications presented have been adapted from the API (Sittig, 1977)

Mill category: I - integrated, N - non-integrated

Pulping. K - kraft; S - sulfite, NS - neutral sulfite; G - groundwood; TMP - thermomechanical; R - recycled paper board, DI - deinking

Swd - softwood; Hwd - hardwood

Bleaching. U - unbleached, B - bleached

Product categories: A - newsprint, B - printing, writing and related; C - packing and industrial;
D - tissue; E - construction grades; F - paperboard; G - market pulp

Location	Mill Category	Pulping	Bleaching	Product Category							Production Capacity	Effluent Treatment
				A	B	C	D	E	F	G		
Brampton (1)	I	G,R	U					X			200 t/day	N/A
Brantford (1)	N					X					N/A	Municipal sewer
(1)	N			X		X					185 t/day	Primary clarifier to Mun. sewer
Cornwall (1)	I	K Hwd	U, B		X	X					800 t/day	Primary clarifier
Dryden (1)	I	K Swd	B		X					X	800 t/day total with 300 t/day market pulp	Primary clarifier Secondary aeration
Espanola (1)	I	K Hwd/Swd	U, B		X	X	X			X	1,000 t/day total with 800 t/day market pulp	Primary - settling basins Secondary - aerated lagoon
Fort Frances (1)	I	K,G SWD	U, B		X					X	785 t/day gwd papers 225 t/day blched kraft market pulp	Primary clarifier -bark plant; primary clarifier -paper mill Secondary - aerated lagoon
Glen Williams (1)	N					X					250 t/day	N/A
Huntsville (1)	N						X				100 t/day	Primary clarifier, secondary polishing basin, Tertiary - percolation beds

TABLE 2: (CONT'D)

Location	Mill Category	Pulping	Bleaching	Product Category							Production Capacity	Effluent Treatment
				A	B	C	D	E	F	G		
Iroquois Falls (1)	I	S, G, DI Swd		X	X						225 t/day sulfite, 640 t/day gwd 120 t/day deinking	Primary clarifier
Kapuskasing (1)	I	S, G, DI Swd		X							200 t/day sulfite, 700 t/day gwd, 120 t/day deinking	Primary clarifier
Kenora (1)	I	S, G		X	X						240 t/day sulfite, 700 t/day gwd	Primary clarifier
Marathon (1)		K Swd	U, B							X	550 t/day market pulp	Primary clarifier
Mississauga (1)	I	R	U						X		346 t/day recycled board	Primary clarifier, secondary settling municipal sewer
Napanee (1)	I	R	U			X			X		230 t/day board	
North Bay (1)	I	G	U			X					130 t/day	Primary and secondary
Ottawa (1)	N				X						180 t/day	Primary with sanitary
Red Rock (1)	I	K, G Swd	B						X		875 t/day	Primary clarifier
S.S. Marie (1)	I	G			X						465 t/day	Primary clarifier
Scarborough (1)	I	R, DI					X		X		500 t/day linerboard, 60 t/day tissue	Primary clarifier
Smooth Rock Falls (1)		K Swd	B							X	358 t/day chlorine free pulp	Primary clarifier

TABLE 2: (CONT'D)

Location	Mill Category	Pulping	Bleaching	Product Category A	B	C	D	E	F	G	Production Capacity	Effluent Treatment
St. Catharines (1)	N			X		X					250 t/day	Primary clarifier
(1)	N						X				115 t/day	Primary clarifier
Sturgeon Falls (1)	I	NS, R							X		260 t/day recycled corrugating	Primary - flotation clarifier
Terrace Bay (1)		K Swd, Hwd	B							X	680 t/day market pulps	Primary clarifier, secondary aerated lagoon
Thorold (1)	N					X		X	X		350 t/day	Primary clarifier
(1)	N				X						290 t/day	Primary clarifier, secondary biological
(1)	I	G				X		X			90 t/day	N/A
(1)	I	G, CTMP, DI Swd		X							450 t/day TMP, 620 t/day deinking	Primary clarifier, and secondary biological
Thunder Bay (1)	I	G, CTMP Swd	U	X							385 t/day	Primary clarifier, secondary settling ponds
(1)	I	S Swd		X							500 t/day	Primary clarifier, two lagoons (Mill is idle)
(1)	I	G, K, DI Swd, Hwd	B	X							1300 T/day recycle-content news 1100 bleached kraft market pulp	Primary clarifier, secondary biological
(1)	I	G Swd			X						460 t/day	Primary clarifier, lagoon
Toronto (1)	N						X				265 t/day 400 t/day	Municipal sewer
(1)		R							X			Municipal sewer
Trenton (1)	I	NS Hwd							X		420 t/day	Closed - cycle
Whitby (1)	I	DI		X			X				90 tons/day tissue 400 T/day newsprint	Primary clarifier, secondary biological

example. In most cases groundwood pulp is blended with pulps from other processes. Combinations of different pulping processes at individual mills lead to variations in the composition and properties of sludges, and, thus, underscore the need to assess prospects for sludge use on a mill-by-mill basis. Moreover, the combined pulping systems employed at many of the mills complicate the characterization of sludges with respect to kraft, sulfite, groundwood or other processes.

At the time of writing, there were six mills in Ontario with deinking capabilities. A seventh operation suspended deinking operations in late 1994. Of the six deinking operations, only two rely exclusively on deinked secondary fibre.

6. MANUFACTURING PROCESSES

The purpose of this section is to briefly summarize the main manufacturing processes in paper production, product lines, effluent sources and solid constituents. The material losses determine the physical, and, to a large degree, the chemical properties of primary clarifier sludges, which, in turn, would affect potential sludge uses. Details on the unit processes, including pulping operations, are presented in Appendix 1. The bulk of the information presented in this section and Appendix 1 was derived from the works of Sittig (1977), and Smook (1982).

Figure 4 presents a generic process flow diagram for pulp and paper production. Integrated pulp and paper mills include all of the unit processes shown, while non-integrated paper mills are limited to the preparation of market pulp and paper making. Pulp mills exclude paper making processes. Table 3 summarizes the major pulp and paper groups, product lines, pulp yields and sludge output.

6.1 Debarking

Bark is an undesirable component of harvested pulpwood and is typically removed before further processing. Mechanical and hydraulic methods are the principal debarking processes. Hydraulic debarking is generally restricted to West Coast operations. Elsewhere, debarking is accomplished in barking drums by either dry or wet processes. In both cases, the rotating action of barking drums and friction between logs represent the primary mechanisms for removing bark. In wet drum barkers, jets of water are used to loosen bark and to enable removal. Dry drum barkers do not yield effluents, and recovered bark is suitable for combustion without further treatment. In contrast, wet drum barkers

Figure 4: Generic process diagram for pulp and paper production.

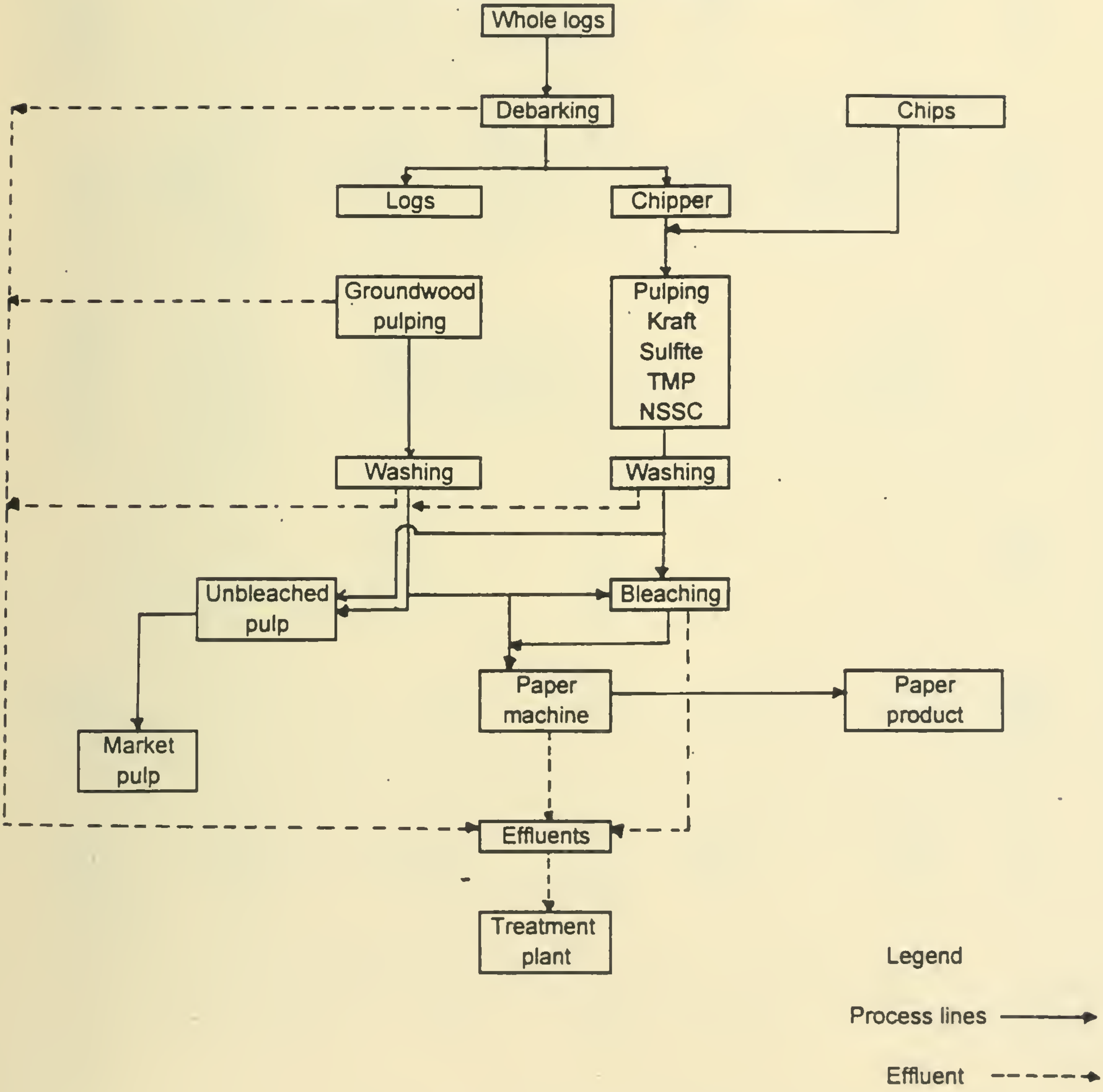


Table 3: Summary of mill process and production types, pulp yields, products and waste by-products.

Integrated pulp and paper mills

Pulp classification	Process	Feedstocks	Pulp yields	Pulp strength	Use	Products	Sludge output
Mechanical							
	Groundwood	Wood bolts or debarked logs usually softwoods	95 %	low	usually mixed with chemical or TMP pulps	Newsprint Magazine Catalog Tissue and toweling Carton board Container board Building board Insulation board	up to 50 Kg/ADT of product mainly as fibres
	TMP	Chips, usually softwoods	90-95 %	medium to low		Newsprint Magazine	up to 50 Kg/ADT of product fibres
Chemical							
	Kraft	Chips - hardwood and softwood	40-50 %	High for softwood Medium for hardwood	High yields used for container board Lower yields for other papers Often mixed with other pulps, eg groundwood	Strong wrapping Container board Book Newsprint Bond and writing High grade magazin	30 Kg/ADT of product as solids Dissolved solids Fibre High ash in bond, writing and fine papers
	Sulfite	Chips - predominantly softwoods	45-50 %	medium to high for softwoods low to medium for hardwoods	Often mixed with other pulps, eg groundwood	Newsprint Book and magazine Wrapping Writing Bond	30-40 Kg/ADT of product as solids Fibre Dissolved solids High ash in bond
	Semichemical	Chips - softwood and hardwood	60-80 %	Low to medium	Alone in corrugation Bleached pulps mixed with other pulps for other products	Corrugating medium Food and specialty boards Magazine Industrial Newsprint	30 Kg/ADT of product Fibre
Deinking		Waste paper - board newsprint, bond ledger	75-85 % based on waste paper contents	Low to medium	Alone in tissue and some newsprint combined with other pulps	Tissue Newsprint Writing papers	160 Kg/ADT of waste news up to 300 Kg/ADT for tissue and bond

yield solids which require dewatering and/or pressing before combustion, and effluents which are difficult to treat. Many mills have adopted dry debarking systems.

Whole debarked logs are used in groundwood pulping, while other mechanical (thermomechanical) and chemical pulping processes rely on chips. Chipping is a dry process. Chips undergo washing and screening to remove fines, grit and dirt before pulping.

6.2 Pulping Processes

Of the pulping categories identified in Table 1, groundwood, thermomechanical, kraft, sulfite, semi-chemical, recycled container board, and deinking operations are represented in Ontario, and are outlined below.

Mechanical pulping

Groundwood: Stone groundwood pulping is the oldest form of mechanical pulping. Whole logs are pressed against a rotating grindstone which tears the wood fibres from the logs. Water is applied to lubricate the grindstone and also to remove fibres. Large fibrous solids are recovered and processed in a reject refiner. Fine fibres are the dominant solid components in sludges from groundwood operations.

Groundwood pulps are frequently blended with kraft, sulfite and thermomechanical pulps to improve strength and sheet qualities for some grades of paper.

Thermomechanical: Refiner mechanical pulping (RMP), also referred to as refiner groundwood ,was introduced in the late-1950s to early 1960s. Thermomechanical pulping (TMP) has replaced RMP processes since the

1970s. RMP pulping involves the heating (with steam) under atmospheric pressures to soften wood chips before defibration using disc refiners. In contrast, the first stage, and perhaps the second stage, of the TMP process involves heat and high pressures to soften the chips. Although pulp yields are lower for TMP processes, pulp and paper qualities are higher relative to those from groundwood and RMP processes.

The principal effluent sources from TMP processes include pulp washing, screening and cleaning operations. Wood and partially delignified cellulosic matter constitute the major solid fractions in sludges from TMP operations.

Chemical Pulping

Kraft process: Kraft pulping process represents the dominant form of chemical pulping. Wood chips are subjected to "full cooking" in alkaline solutions of sodium hydroxide and sodium sulfide. Due to the common use of sodium sulfate in pulping liquors, the kraft process is synonymous with sulfate pulping defined by the API (Table 1).

Valuable pulping chemicals are recovered from spent pulp (black) liquors. Washing of pulp (brown stock washing) is completed to remove residual black liquor, a portion of which may be subject to recovery, or is otherwise discharged to the effluent treatment plant. Dissolved solids and fibre are the main constituents in kraft pulping effluents.

Sulfite Pulping: Chemical sulfite, also referred to as acid sulfite, pulping involves the cooking of wood chips under heat and pressure in a solution containing sulfurous acid and bisulfite. Solution pH is dependent on the ratio of acid to bisulfite, and varies from 2.5-6.0 depending on process and product lines. Ammonium, calcium, magnesium and sodium are the main ionic bases used in sulfite pulping, of which the latter two are represented at mills in Ontario. Spruce, fir and other low resin woods are well suited to sulfite pulping. In contrast to kraft pulps, those derived from sulfite pulping possess higher degrees of brightness and require less intense bleaching. Pulp washing, for the removal of liquor residues, and screening represent the principal effluent source. Fibres and dissolved organic compounds represent the major components in sulfite pulp effluents.

Semi-chemical pulping: Neutral sulfite semi-chemical (NSSC) pulping involves the cooking of chips in sulfite solutions with ammonium or sodium bases. Much of the lignin in the wood chips is retained. After cooking, the chips are defibrated mechanically to yield pulp. NSSC operations have generally achieved a high degree of closure and generate limited quantities of effluent. Spent liquors have been used for some time as dust control agents/binders for unpaved roads. The few available samples of screenings/sludge obtained from NSSC mills contain bark and wood fines/fibre, grit, dirt and other solids.

Recycled Paper and Deinking Operations

Waste paper board, corrugation and other papers have been recycled for some time for the production of liner board and other board products. Newsprint recycling has been practised for decades. Waste paper and board products have also been repulped and defibrated for use in construction grade products such as saturating papers, and roofing felts.

Waste papers are fed to a pulper with a ragger and/or junker to recover the usable fibres (long) and remove physical contaminants - glass, metals, plastics, fabrics and glues, for example. Deinking is not a requirement for the manufacture of board from recycled fibre. Pulp washing and screening represent the primary sources of effluents, and wasted solids, primarily fibres. Overall, the pulp yields are high, and sludge output is low.

Deinking: Deinking operations essentially involve laundering processes (Howard, 1994) - washing and flotation. Waste paper is fed to a pulper equipped with a ragger and junker for the removal of physical contaminants.

In washing systems, the raw pulp is transferred to a process train for multiple washing and cleaning stages. Detergents/surfactants, dispersants and foaming agents are added on the front end of the process to remove and disperse ink solids. The pulp is then transferred to two or three washing stages for removal of sand, grit, dirt and coarse ink solids. At the end of the washing sequence, the deinked pulp is sent for bleaching, where appropriate, mixed with other pulps (e.g. TMP, groundwood, kraft and sulfite) and transferred to the paper making stage.

Although flotation deinking processes have been accepted in Europe, they have only recently been adopted at deinking mills in North America. In the flotation system, repulping and deinking are completed simultaneously in the pulper, and avoid the extensive washing sequences.

The goal of deinking operations is the recovery of usable long fibres. Fine fibres, which have a detrimental effect on drainage in the paper machine, are removed along with clay fillers and coatings, ink solids and other contaminants.

Pulp yields from deinking operations vary from 75-85% (Table 3), with respect to recoverable fibre. The highest yields are associated with newsprint production, while the lower yields are obtained from bond, ledger and other similar paper products.

Wasted solids from the deinking of newsprint are dominated by cellulosic fibre (60%), while clay fillers and coatings from fine papers, ledger stock and bond may amount to 60% of the sludge matrix.

Pulp Bleaching

Bleaching processes are used to brighten and/or delignify pulps for specific paper products. Softwood (spruce, fir) pulps from mechanical pulping are sufficiently bright for use in newsprint. For these pulps, zinc hydrosulfite may be used as a bleaching agent. Sulfite pulps, depending on product lines, may undergo a single chlorine, hypochlorite or oxygen bleaching stage. Kraft pulps are generally coloured (brown) and require multiple stages of bleaching, each of which is separated by alkaline extraction or washing.

The primary source of effluents from bleach plants is derived from the washing stages. These effluents may contain residuals of bleaching chemicals, dissolved organics (lignin) and some fibre.

Paper Making

Bleached and unbleached pulps undergo further preparation by addition of water to obtain the appropriate consistency, sizing and fillers. The prepared pulp is deposited on the wire or web from a stock chest. Water is removed from the paper sheet by pressing between rollers, and also by steam heat. Portions of the white water from the cleaning processes and the paper machine are returned to the process for reuse. Machine screenings, centricleaners and pressing processes yield effluents containing fibre, clay fillers and other additives.

7. EFFLUENT TREATMENT

Previous sections identified the principal sources of effluents associated with wood preparation, pulping, pulp bleaching and paper making. Removal of suspended solids, dissolved solids and biological oxygen demand (BOD) is required before effluent can be discharged from a mill.

In many cases, effluent pre-treatment is required to remove grit, coarse solids and other debris to minimize abrasion and damage to pumps and other appurtenances in the treatment plants. Also, effluents from chemical pulping and bleaching operations require pre-treatment to neutralize acids and alkalis. Finally, effluent preparation and equalization is required to moderate flow, and reduce potential effects of surges and overflows on treatment system upset.

Three general treatment processes are employed at pulp and paper mills, in varying configurations. These are identified as follows:

1. Primary clarification - removal of suspended solids
2. Secondary treatment - removal of biodegradable matter and fine solids
3. Tertiary treatment - removal of colour, odour, taste and toxicity.

Treatment systems installed at pulp and paper mills were designed to treat all, or part of the effluent generated. In this regard, sanitary sewage is usually excluded from mill effluent treatment systems, and processed separately. Mills situated in urban areas discharge sewage to municipal plants, while, in other areas, sewage is processed in lagoons. At newer mills, effluents from the various sectors within a mill may be segregated for separate treatment, to reduce treatment costs. For example, separate treatment systems may be installed to handle effluent from woodrooms relative to pulping and paper making operations. Effluents from kraft bleach plants may by-pass primary treatment due to low suspended solids levels. Alternatively, separate treatment may be provided to remove alkaline solids from kraft operations.

Figure 5 presents a generalized process diagram for a typical combined primary clarifier and secondary biological effluent treatment system. With few exceptions, Ontario mills possess primary treatment systems in the form of clarifiers and or lagoons, settling basins and aerated lagoons which provide primary and secondary treatment. A small number of mills rely on combined primary clarifier and secondary biological treatment systems. Due to recent effluent quality regulations, many mills will be upgrading treatment plants to include primary clarification and secondary (biological) systems.

Only one Ontario mill relies on tertiary treatment, in the form of filter beds.

Primary Clarification

Primary treatment is accomplished by gravity clarifiers, settling basins or lagoons, and, in some cases, air flotation systems. Primary effluent treatment removes 80-95% of the settlable suspended solids, but only about 10% of the BOD, the latter of which is associated with soluble or dissolved organic matter. Fine suspended solids may be captured by adding flocculants such as alum, ferric chloride or polymers.

Effluent is fed into the centre of the clarifier, which flows radially outward towards an overflow weir. Effluent from the overflow may be recycled back into the clarifier, equalization tank or system, and/or the secondary system. Settled solids are raked towards the centre (bottom), drawn-off, and, subsequently, dewatered for disposal.

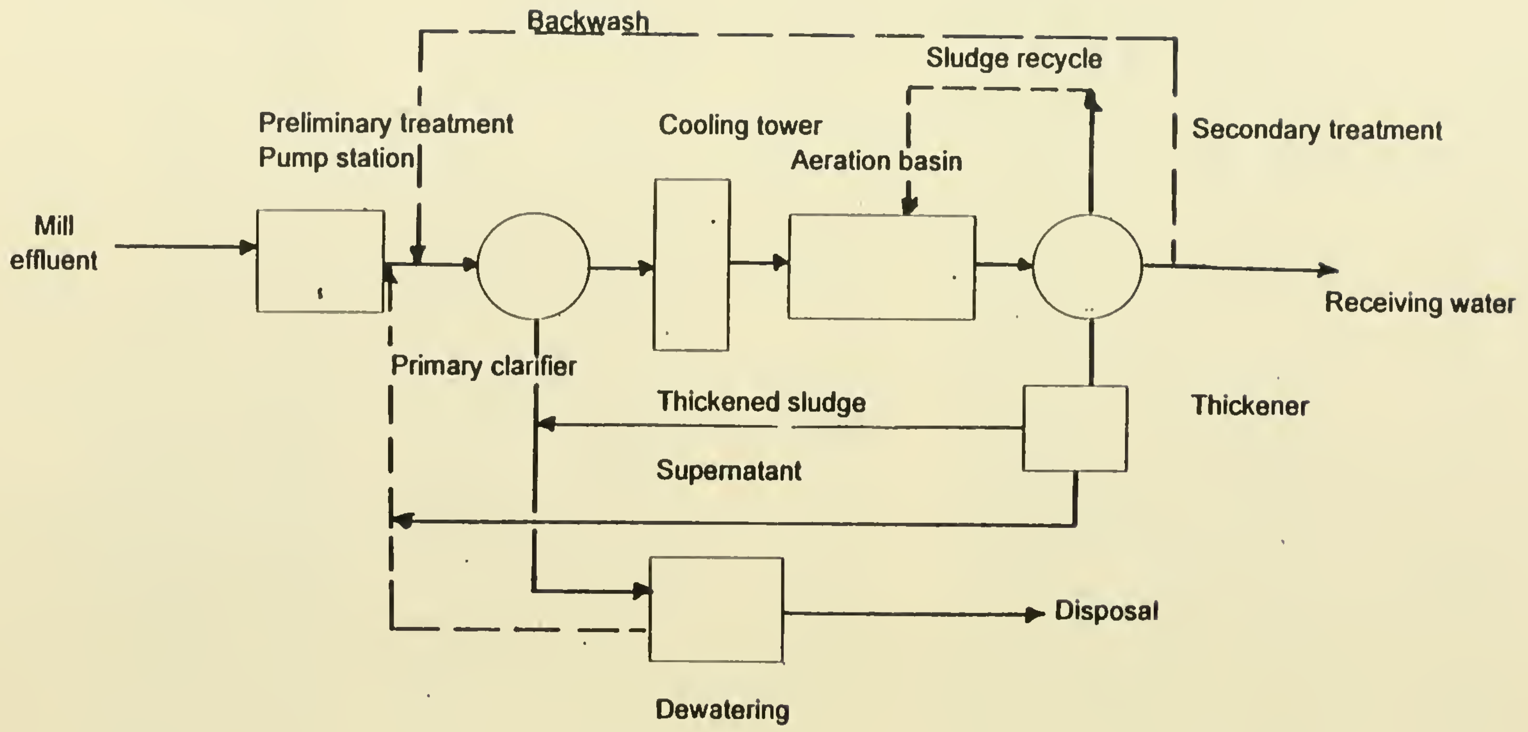


Figure 5: Combined primary and secondary treatment plant process diagram.

Settling basins or lagoons are usually constructed by excavation and earthworks, with an inlet and outlet. Settling basins may be lined with low permeability materials, such as clay or synthetic membranes, or unlined to allow for gradual percolation of wastewater. Unlike common clarifier systems, the removal of accumulated solids, or sludge from lagoons requires the use of excavation equipment. Also, dewatering of lagoon sludges cannot be conveniently accomplished.

Secondary Treatment

Secondary biological treatment systems are designed to remove dissolved organic matter through biological action. The most common secondary treatment systems are aerobic in nature and depend on the addition of air, oxygen and/or agitation to maintain an aerobic consortium of microorganisms. Aerated lagoons have served the same purpose and have been widely adopted. However, activated sludge and other aerobic treatment systems are being added to existing treatment plants to achieve effluent regulations. Anaerobic digestion processes, although not widely accepted, have been examined as a means of reducing sludge output.

The essence of aerobic treatment systems is heterotrophic microbial activity for the decomposition of various organic substrates. Heterotrophic microorganisms rely on organic carbon as the essential energy source (Alexander, 1977). The decomposition of organic matter and, hence, the use of C, depends on the structure and availability of organic substrates and nutrients, principally nitrogen and phosphorus. Simple sugars, amino acids and sugars, proteins and other low molecular weight organic substrates are readily assimilated, provided sufficient N and P are also available, in the proportions of C:N of 20-30:1, and N:P of 4-8:1. Polysaccharides such as cellulose and other polymerized organic materials are not readily available, their decomposition being dependent on initial enzyme attack, and subsequent assimilation of simpler molecules. Highly polymerized lignin and high-molecular weight compounds such as terpenes and resin acids are typically resistant to biological degradation, and may, therefore, persist through secondary treatment processes.

Microbes generally become attached to organic substrates provided nutrients are available (Pethica, 1976; Costerton et al, 1987). Adherent masses or flocs of microbial cells are more efficient at capturing nutrients in solution, and agitation and aeration provide the essential contact between substrates, nutrients and microbial masses to enable decomposition. Flocs of biomass gradually settle out of suspension. However, a high percentage of the biomass and fine solids remains in suspension. Removal of these suspended materials and dewatering of secondary sludges can be difficult without substantial additions of expensive polymers. Due to the difficulties in dewatering secondary paper sludges alone, the common practice has been to blend primary and secondary sludges before dewatering.

With the exception of settling basins and/or aerated lagoon systems, secondary treatment systems are usually combined with primary clarification. High suspended solids loadings cannot be effectively accommodated or treated by secondary systems alone. Primary treatment systems provide a partial buffer to surges, spills and shock loads of effluent that could detrimentally affect the biological activity and, hence, treatment associated with secondary treatment systems.

Sludge Output

Figure 6 presents a comparative summary of primary (Figure 6a) and secondary (Figure 6b) sludge generation rates (dry weight basis), as percentages of total paper production. The data presented in Figure 6 were obtained from NCASI (1992), the results of a 1989 U.S. mill survey. This represents the most recent statistical information available. No similar data are currently available for Canadian mills.

The highest primary sludge generation rates shown in Figure 6a were associated with deinking operations. These data would reflect the higher losses of fine non-recoverable fibres and the removal of clay fillers, coatings, inks and other matter during repulping. Although fibre yields are low for chemical pulps (kraft and sulfite), the vigorous attack of wood fibres by chemical pulping liquors results in higher losses relative to soluble solids, and, ultimately, lower primary sludge output from chemical pulps and papers.

Secondary sludge generation rates (Figure 6b) show considerable variability. The high secondary sludge output evident for the bleached kraft and sulfite categories, would be due to higher biomass production in response to the higher dissolved solids concentrations in effluents from these operations. The difference in secondary sludge generation rates between bleached and unbleached kraft categories reflect the additional delignification and solubilization of organic materials associated with bleaching, and, hence, higher loadings of dissolved solids entering secondary treatment systems.

Although the data presented in Figure 6 show relative quantities of primary and secondary mill sludge generation rates, they do not provide a reliable indication of the quantities of material that are involved, especially on an "as-received" basis. Unfortunately, comprehensive data on sludge generation rates are not readily available, in part because of a reluctance to release such information by individual mill/company representatives.

Figure 6a.

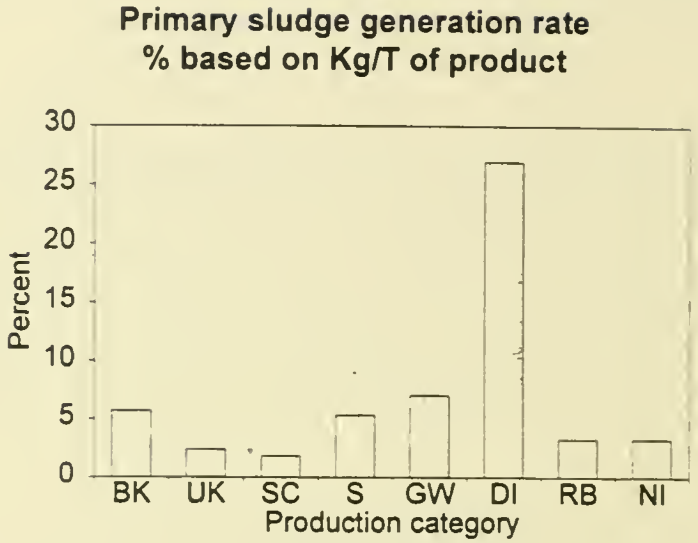


Figure 6b.

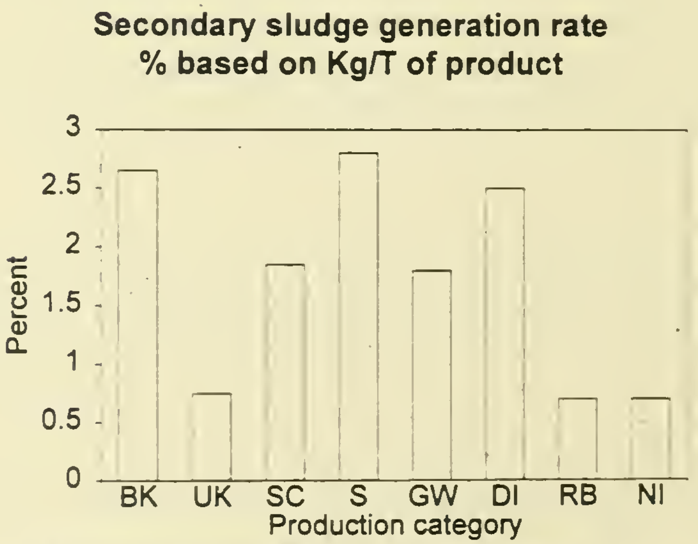


Figure 6: Sludge generation rates from primary clarifier (a) and secondary treatment systems (b). BK - Bleached kraft; UK - Unbleached kraft; SC - Semi-chemical; S - Sulfite; GW - Groundwood DI - Deinking; RB - recycled paperboard; NI - Nonintegrated. Generation rates are based on dry weights for sludge and product.

On a wet weight basis (30-40% total solids - with a median of 35%), sludge output at Ontario mills (ORTECH, confidential sources) varies from about 20 T/day (primary sludge only) for small non-integrated paper mills to 300 T/day (combined primary and secondary sludge) for deinking operations. On an oven dry basis, the corresponding sludge outputs would amount to 7-100 T/day. For raw undewatered sludge with a consistency of 5.0% total solids, sludge output would range from 140-2,000 T/day. The quantities of dry, wet-dewatered, and raw-undewatered sludge, generated at individual mills, would have a significant impact on capital equipment required, operating and maintenance costs, and manufacturing capacity relative to commercial uses of paper industry sludges.

8. PAPER INDUSTRY SLUDGE COMPOSITION

Comprehensive data on the physical and chemical composition of paper industry sludges are limited. Most of the analytical work and data have been compiled for land application purposes. The NCASI (1984) compiled data for a variety of chemical components in paper sludges, in general to assess the suitability of paper sludges as soil amendments. Extensive paper sludge data have been compiled for Ontario mills that have established land application programs. Research projects on alternative uses have provided sludge analyses, although the sets of parameters appear to be limited to single samples and specific applications.

Table 4 presents a summary of comparative compositional data for sludges from Ontario mills. The database for Sludge A amounts to approximately 120 samples, collected as monthly composites since 1984; for Sludge B, 80 monthly composite samples; for Sludge C, 24 monthly composites; and, for Sludge D, 12 monthly composites. The remaining sludge data sets were derived from single samples. Interestingly, the most extensive data on paper sludge composition were derived from deinked secondary fibre operations. No similar data are available from groundwood or kraft operations.

Physical Composition

Total solids (TS) and volatile solids (VS) contents shown in Table 4 represent general physical properties of paper sludges. As shown, TS values are highly variable with a range of about 17-53% on a dry weight basis. VS values also vary widely among the different sludges. High organic matter (VS) concentrations were encountered in primary sludges from paperboard and newsprint (sulfite). The solid fractions in the primary sludges are predominantly fibre, clay fillers and coatings, inks and

TABLE 4: COMPARATIVE CHEMICAL DATA FOR SECONDARY AND VIRGIN FIBRE PAPER SLUDGES

All concentrations in mg/kg except as noted

Sources: ORTECH records (confid. client base).

Parameter	**TMP/deink** News A	**Nonintegrated/deink** Fine B	**Deink** News/Tissue C	**Deink** Tissue D	**Recycled** Board E	**Nonintegrated** Specialty F	**Sulphite** News G	**Guideline** OMAF, MOEE 1992
Treatment	Prim/Second	Prim/Second	Prim/Second	Prim	Prim	Prim	Prim	
pH	6.5-8.5	6.22-7.98	6.15-9.10	4.27-8.46	7.49-7.6	5.88	5.02	
Total Solids %	25.8-37.1	25.9-39.6	30.22-48.72	29.70-53.01	17.6	33.42	27.75	
Volatile Solids %	65.02-76.9	49.2-65.7	50.70-88.97	46.66-93.86	83.56	72.12	95.8	
TKN	7,670-24,300	6,840-42,900	1570-5,600	800-5,930	9,790	1170	2,160	
Ammonia	76.7-1,280	3,020-9,360	<10-130	<10-56	86.5	111	389	
Nitrate	0.5-9.5	680-14,800	<1-5.6	<1-20.5	11.5	10.4	0.14	
Chloride	29.6-183	124-823	57-215	50-1,730	670	342	29	
Sulphate	166-730	611-4,000	414-1,080	<10-1,170	418	8,550	2840	
Calcium	7,000-12,900	1,400-25,900	4,800-51,600	720-141,000	20,600	5,090	6,200	
Magnesium	900-1,600	710-1,700	450-890	180-1,730	520	1,830	360	
Sodium	755-1,900	350-780	470-1,100	120-1,400	880	220	2740	
Potassium	150-1,100	15-340	38-331	47-300	<200	350	205	
Phosphorus	814-2,490	320-1,200	87-830	250-1,120	140	260	<50	
Arsenic	<0.2-1.3	<0.5-3	<0.3	<0.3	<0.5	0.873	<0.2	170
Cadmium	<0.2	<0.5-0.83	<0.3-1.0	<0.3-0.5	<0.5	<0.5	<0.5	34
Cobalt	<0.8-1.1	0.8-1.1	<0.8-1.9	<0.8-2.6	<1	<1	<0.5	340
Chromium	9.4-21	<1-48	5.9-18	5.4-19	3.8	18	2.4	2800
Copper	140-260	<3-81	106-462	28-78	25	27	7.2	1700
Mercury	<.002-0.18	<0.02	<0.1	<0.1	<0.1	<0.1	0.01	11
Molybdenum	<0.5-2.45	<0.5-4.4	<0.5-3.2	<0.5-5.2	<1	2.5	<2	94
Nickel	<1.0-12	<1-8	1.4-6.9	1.2-5.7	<1	4.6	1.6	420
Lead	<2.0-11	<0.1-26	<5-23	<5-13	9.4	32	3.2	1100
Selenium	<0.4-0.21	<0.2	<0.2	<0.2	<0.5	<0.5	<0.5	34
Zinc	40.7-105	<8-440	81-240	30-125	36	51	33	4200
Phenolics	0.067-4.3	0.05-0.91			0.21	0.32	41.1	
Phthalate-esters	<2-12	<1-13.8			8.9	5.6		
Benzene	<0.2	<0.2			<1	<1	<1	
Toluene	<0.4-2.3	<0.2			<1	<1	<1	
Xylene	<0.2	<0.2			<1	<1	<1	
PCB	0.01-0.40	<0.4-6.81			<0.01	0.07	0.1	0.5
dioxin (ppt, TEQ)	3-7	4-48	2.3-13.4	3.6-17.3				

miscellaneous inorganic and organic solids. Sludge A is a combined primary and secondary sludge with 2.5:1 proportions of primary to secondary material. Sludge B is a 10:1 blend of primary to secondary sludge solids. Proportions of the primary to secondary sludge in Sludge C were highly variable with a range of 3.0-20:1.

The quantities of secondary sludge solids and nutrients, principally nitrogen and phosphorus, can have a major effect on the compositional quality and stability of combined primary and secondary sludge. For example, the secondary sludge component of Sludge A contains up to 4.0% N (dry weight basis) and a viable microbial population, that results in a rapid onset of thermophillic activity after the mixed primary and secondary sludge is dewatered. Active decomposition will reduce the sludge mass and ultimately yield humic materials, essentially altering the composition of the original sludge matrix. Large static piles of sludge turn anaerobic fairly rapidly, with resultant releases of odorous compounds (ammonia, sulfides, mercaptans, fatty acids). Depending on sludge moisture content (e.g. >70%) leachate may be generated due to the putrification and fermentation of the organic solids.

The consistency of paper sludges is dependent on moisture content and also the method of dewatering. Raw sludges (primary) contain 3-5% TS before dewatering, and raw secondary sludges may contain 1-3% TS. When the TS level is increased to 20-25%, sludge consistency varies between a wet slurry and cement-like solid. At the 50% TS level dewatered sludge may range from a light, fibrous mat, to hard and brittle agglomerations of 1.0 - 10 cm in diameter. In one sample that was dewatered to 55% TS, the material resembled a hard sheet of fibre board. In the absence of shredding or milling, agglomerated sludge is difficult to mix with other materials to achieve a homogeneous matrix.

Dewatering processes, especially pressing, have an adverse effect on residual fibre quality, and hamper the separation of fibre from ash. This is due to the abrasive action of fine inorganic solids against the fibres, and the embedding of hard material in the fibres.

Chemical Quality

The pH of sludges varies widely from acidic to alkaline. Sludges derived from sulfite operations tend to possess low pH, while alkaline sludges are associated with kraft and some deinking processes. Considerable variations in pH are notable for sludges from deinking operations. This is probably due to variations in chemical residues and waste paper composition, and the use of alkaline surfactants in deinking processes.

Calcium concentrations in the sludges vary substantially, especially for Sludges C and D. Calcium carbonate in the waste papers would account for the high calcium levels. The range of calcium content in Sludge D is substantial and reflects day-to-day variability, relative to properties of the waste paper used, and also production schedules for the newsprint and tissue lines.

Relative to the available guidelines for the land application of sludges in Ontario (OMAF, MOEE, 1992) the concentrations of the 11 trace and heavy elements shown in Table 4 are low. Data compiled by Pridham and Cline (1988) showed that the heavy metal concentrations in paper industry sludges were comparable with those in livestock manures.

Few paper industry sludges have been subjected to comprehensive organic chemical analysis. The NCASI (1984) presented data on the concentrations of various organic compounds including: wood extractives - resin and fatty acids, terpenes, phenolics (lignin); volatile hydrocarbons (benzene, toluene and xylene); chlorinated phenolics; PCB and pesticides;

phthalate-esters; and, surfactants. In general, concentrations of these various compounds have been present in sludges at low levels (NCASI, 1984) and would not constrain their uses as soil amendments, nor in commercial product applications.

The NCASI (1984) reported low levels of chlorolignin and chloroform from bleached kraft operations. These compounds arise from the reactions between organics in the pulp and chlorine bleaching agents. Levels of chloroform as high as 50 mg/kg were reported for raw sludge. Recent changes in bleaching processes and the move away from chlorine and hypochlorite are expected to reduce the formation of chlorinated organic compounds, including dioxins and furans (PCDD/PCDF).

PCB analysis was required because of potential contamination of recycled paper feedstocks by some carbonless copy papers coated with PCB. These PCB coated papers have not been produced since the early 1970s, and, therefore, the likelihood of contamination currently is limited. Detectable PCB residues in some paper sludges were determined by conventional GC/ECD methods. Interference from unidentifiable sulfur compounds led to the development of additional sample cleanup procedures and reanalysis. Results from repeat GC/ECD analysis showed that none of the chromatographic profiles matched commercial Arochlor congeners. Moreover, additional analysis by GC/MS showed that PCB residues were absent with a detectable limit of 0.01 mg/kg (ORTECH, 1987; confidential client).

PCDD/PCDF concentrations as TEQ values for 2,3,7,8 T_4CDD have, in all sludge samples analyzed to date, been <100 ppt. On two occasions PCDD/PCDF concentrations were >15 ppt (24 ppt, and 48 ppt) in samples of Sludge B. These residues were attributed to chlorine bleaching processes. The PCDD/PCDF residues in Sludges A, C and D are presumably derived from waste paper or background sources because these mills do not employ chlorine bleaching processes.

Compositional variability

Harkin (1982), among others, noted that various uses of paper sludges in commercial products have been discouraged by the compositional heterogeneities and inconsistencies of these materials. Significant fluctuations in the physical, chemical and biological properties of paper industry sludges can occur on a day-to-day basis due to the following factors:

(a) Contrasts in constituents in feedstocks, product lines and production schedules for specific products at individual mills

(b) Production system upsets and/or failures, including accidents

(c) Surges, upsets and problems affecting effluent treatment plant operation

(d) Variations in the quantities and proportions of wasted primary and secondary sludge

With respect to deinking operations, substantial variations should be anticipated due to the heterogeneity of waste papers.

Time-series data on the composition of paper industry sludges are not extensive, nor widely available. Land application programs established in Ontario have been accompanied by regularly scheduled monthly analyses of sludge for periods of three to eight consecutive years. These data are presented in this section to highlight compositional variability. However, it is essential to note that the data were derived from deinking operations.

Selected data on the composition of sludges from three operations are presented in Figures 7 and 8, and represent Sludges A, C and D respectively. Table 5 summarizes the mill operations, product lines, effluent treatment processes and sludge output associated with the compositional data.

With respect to the examples presented, raw sludges are dewatered from about 3-5% total solids to 30-40% total solids (weight basis) before disposal at landfills, or land application. Organic matter (volatile solids) and ash contents are mirror images, and define the general physical attributes of these sludges. Calcium, sodium, chloride and sulfate occur at moderate to high levels, due to chemicals used in paper production and thus provide general indications of variations in sludge composition, due to paper production. Alum (alumino-sulfate) is used extensively as a flocculant, and concentrations in paper sludges have varied from 0.2-2.0% in individual samples. However, Al is also present in clay fillers and coatings as alumino-silicates. Concentrations in paper industry sludges have not been subjected to rigorous assessment.

Nitrogen (total Kjeldahl nitrogen - TKN) has been included as a relative index for secondary sludge content. In this regard, wood fibre and cellulosic paper fibres in primary clarifier sludges yield TKN concentrations of <0.3%, while secondary biological sludges can contain up to 7.0% N (Brockway, 1983). The sludge represented by the data in Figure 7 consists of 2.5:1 ratio of primary to secondary sludge, on average, with 1.0% N (dry weight basis). N concentrations >1.0% signify higher proportions of secondary sludge in the matrix. Lower N concentrations would reflect higher proportions of primary sludge solids. The differences or variability in composition based on N content are significant since primary sludge solids are dominated by fibrous (cellulosic) and inorganic

Table 5: Summary of mill type and operations associated with compositional data presented in Figures 7 and 8 (Sludges A, C and D respectively in Table 1).

Mill (From Table 4)	Type	Manufacturing processes	Product lines	Production capacity	Treatment system	Sludge output
A	Integrated	Groundwood pulping Thermomechanical pulping Deinking	Standard and recycled content newsprint	450 T/day TMP 620 T/day deink	Primary clarifier Secondary biological	approx 83 T/day (dry weight) 200 T/day (wet weight) @ 35 % total solids
C	Integrated	Deinking - ledger, bond writing newsprint, magazine	tissue newsprint		Primary clarifier Secondary biological	approx. 100 T/day (dry weight) 280 T/day (wet weight) @ 35 % total solids
D		Deinking - ledger, bond writing	tissue	60 T/day	Primary clarifier	approx. 20 T/day (dry weight) 60 T/day (wet weight) @ 35 % total solids

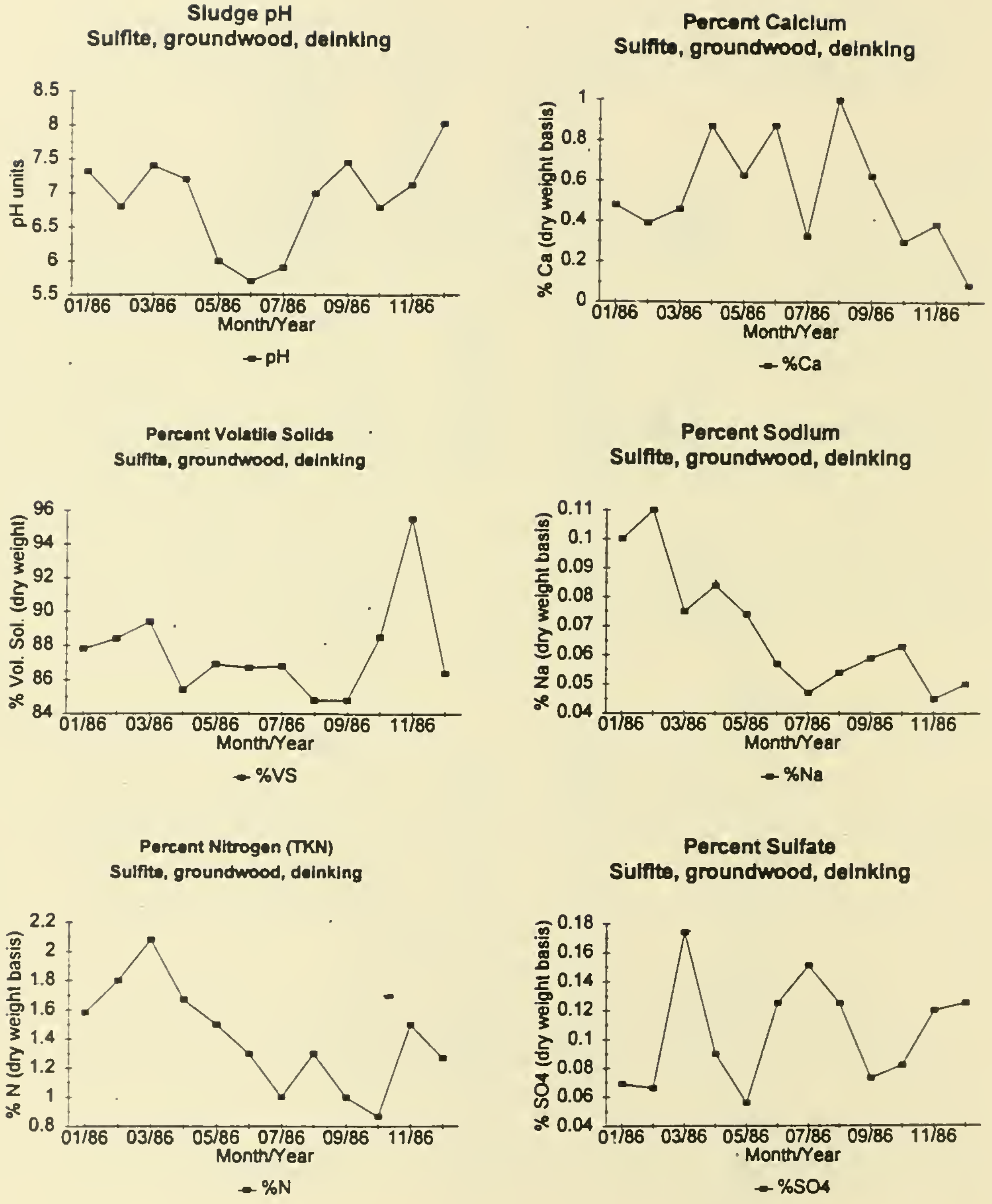
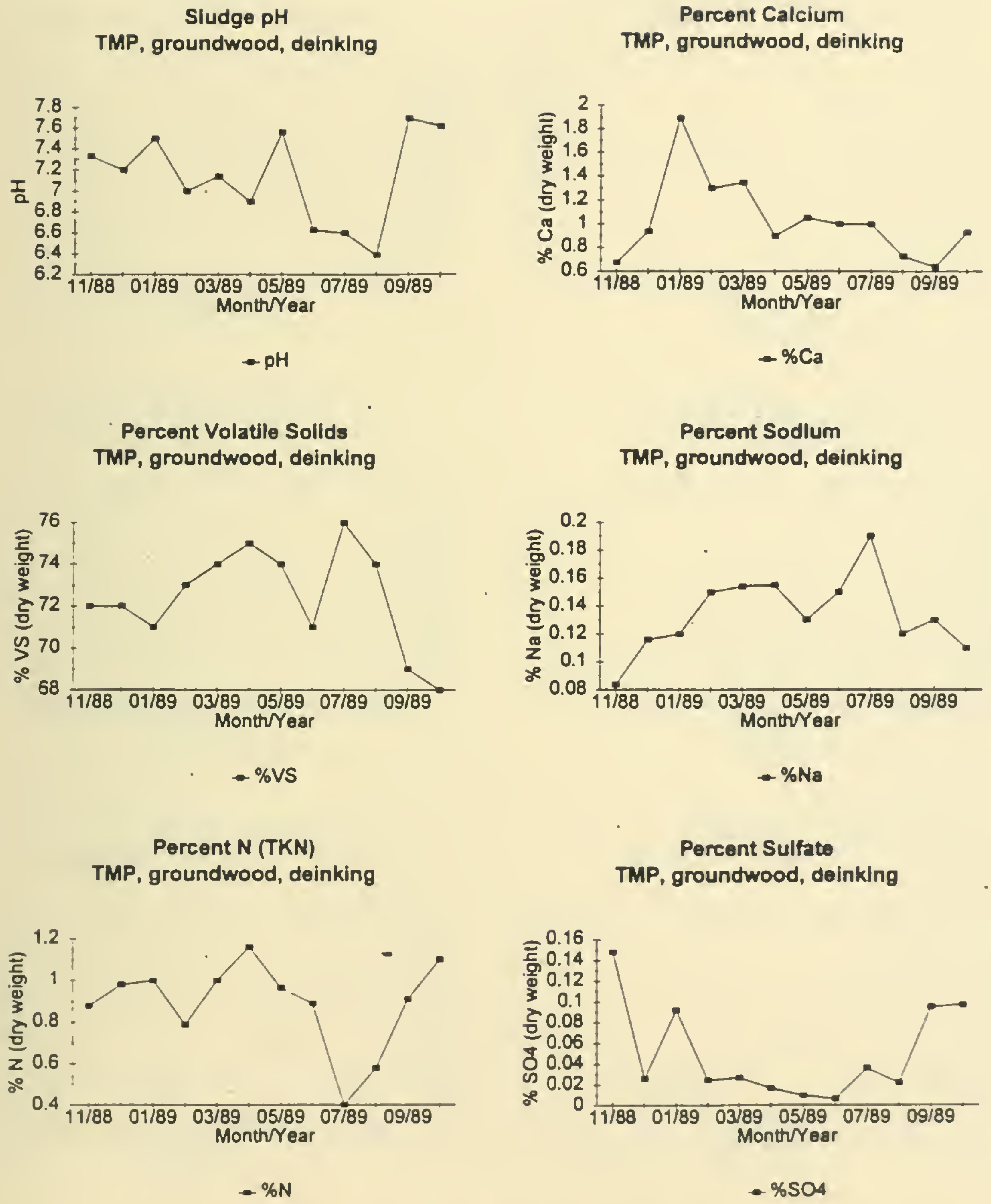


Figure 7a. Variability of selected sludge composition data for 1986. The data represent were from individual samples that were collected on a monthly basis. At the time mill operations included chemical sulfite and deinking processes, with about 30 % secondary fibre content. Effluent treatment involved primary clarification and secondary biological processes.


Sludge pH
TMP, groundwood, deinking

Percent Calcium
TMP, groundwood, deinking

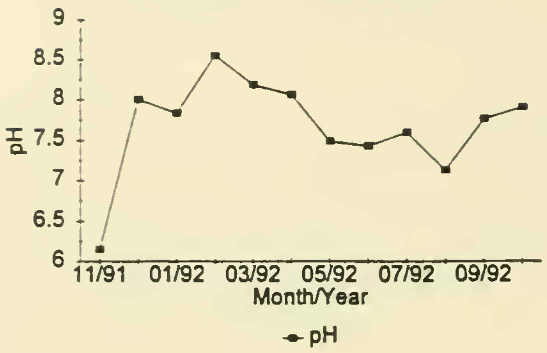
Percent Volatile Solids
TMP, groundwood, deinking

Percent Sodium
TMP, groundwood, deinking

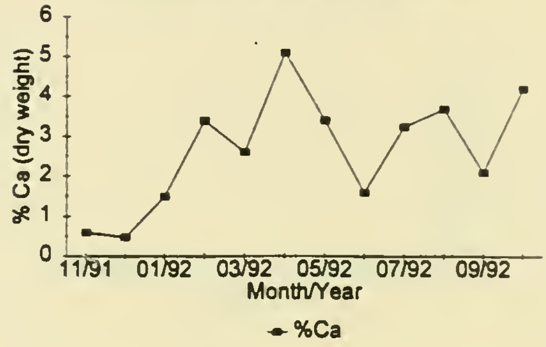
Percent N (TKN)
TMP, groundwood, deinking

Percent Sulfate
TMP, groundwood, deinking

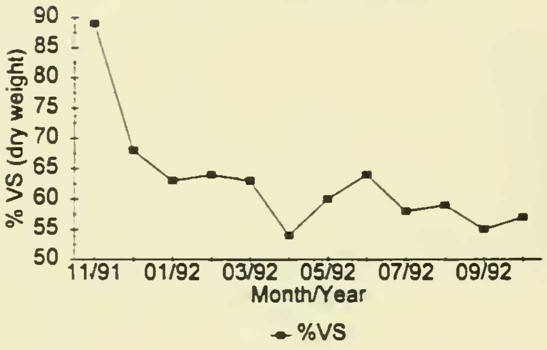
Figure 7b. Variability of selected sludge composition data for 1988-89. The data represented were from individual monthly sludge samples. The mill switched from sulfite to thermomechanical pulping in 1988. Deinking operations account for about 60-70 % of the fibre used. Effluent treatment involves primary and secondary processes.



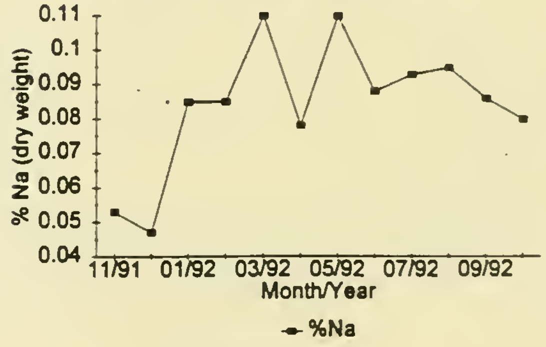
Sludge pH
Newsprint and tissue (100 % deinked)



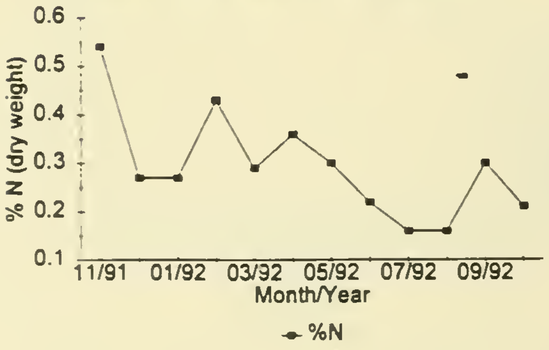
Percent Calcium
Newsprint and tissue (100 % deinked)



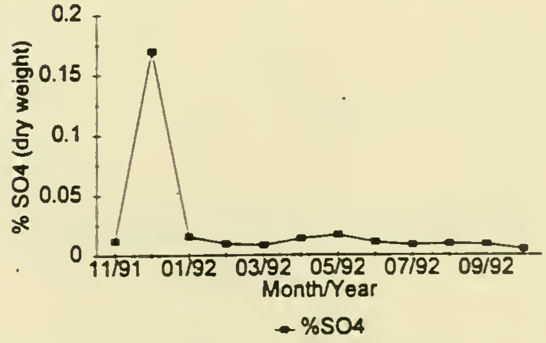
Percent Volatile Solids
Newsprint and tissue (100 % deinked)



Percent Sodium
Newsprint and tissue (100 % deinked)



Percent Nitrogen (TKN)
Newsprint and tissue (100 % deinked)



Percent Sulfate
Newsprint and tissue (100 % deinked)

Figure 8a. Variability of selected sludge composition data from 100 % deinked tissue and newsprint. Combined primary and secondary treatment processes are employed at this mill (Sludge C from Table 2).

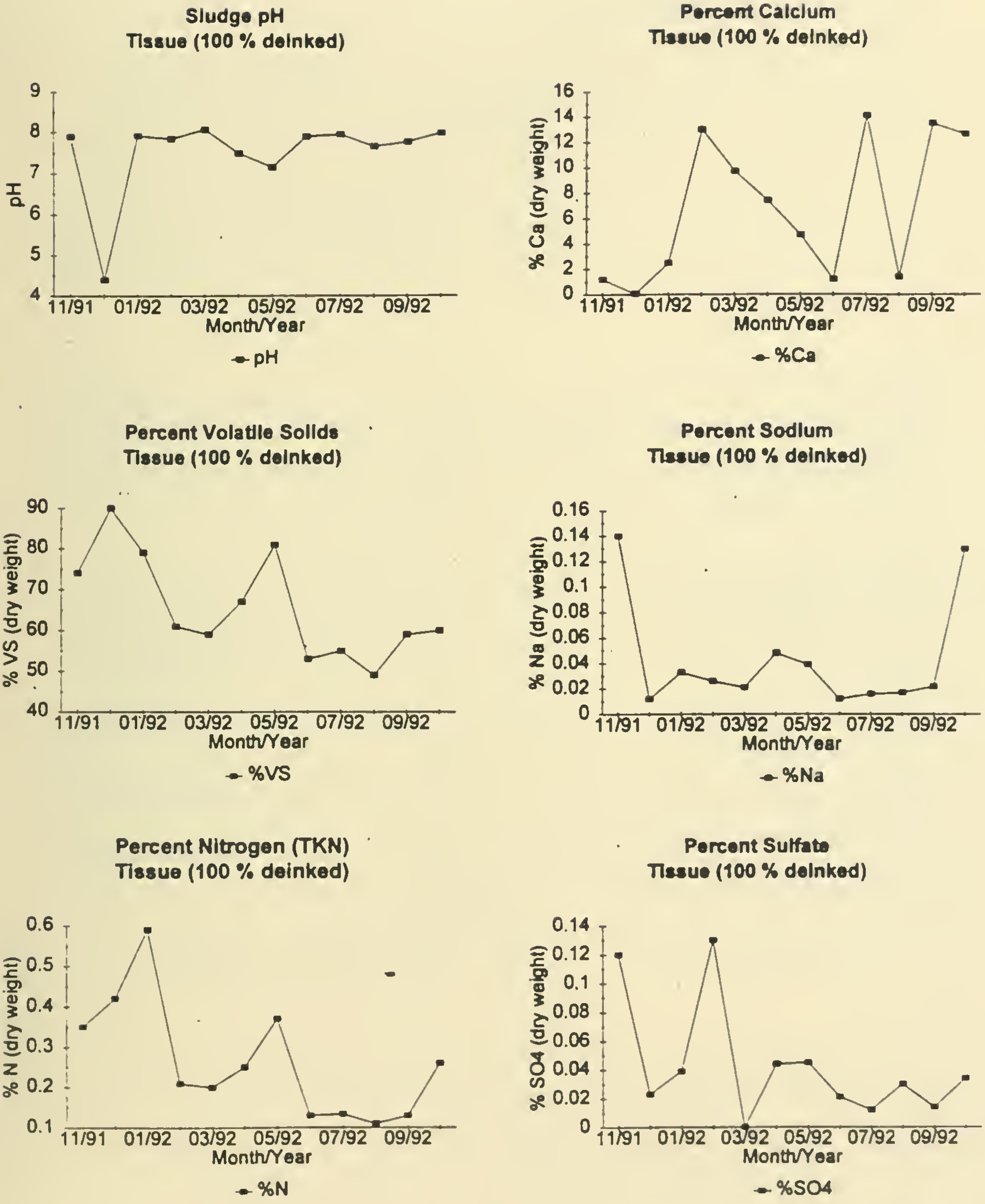


Figure 8b. Variability of selected sludge composition data from 100 % deinked ledger, bond and related papers for tissue manufacture. The treatment process involved primary clarification only (Sludge D, from Table 2).

matter, while secondary sludge solids are comprised of biomass, colloids and limited quantities of fibrous matter. Thus, although two separate sludge samples from the same mill treatment system yield identical organic matter contents, the composition may be radically different due to varying proportions of fibrous organic matter versus non-fibrous biomass and colloids. Variations in fibrous versus non-fibrous matter content could have a major effect on product quality and performance, if fibrous sludge components are targets for use in commercial products.

High losses of fibre and removal of ash (primarily clays), associated with the deinking of ledger and bond stocks, account for higher proportions of primary sludge relative to secondary sludge, and also the low N content of the combined primary and secondary sludge in Figure 8a.

Levels of calcium vary substantially in sludges derived from the recycling of white office, bond and ledger stock, due to variable calcium carbonate contents in waste paper (Figure 8). Sodium levels in sulfite and kraft sludges are moderate, due to pulping chemicals (Figure 7). With respect to the data in Figure 7, higher sodium contents were encountered in TMP-deinking sludge due to the use of various sodium compounds in deinking processes (sodium phosphate, sodium silicate, caustic soda and sodium boro-hydride), as surfactants and dispersants.

9. ALTERNATIVE PAPER SLUDGE MANAGEMENT OPTIONS

Alternatives to the conventional disposal of paper industry sludges are diverse, but can generally be categorized as follows:

1. **Material Recovery and Recycling**

2. **Manufactured Products and Commercial Applications**

Material recovery and recycling is an important consideration relative to the potential uses of paper sludges. In-plant loss reduction and waste minimization involve the capture of materials, including fibre and fillers/coatings, that would otherwise comprise a significant waste fraction. Improvements or optimization of fibre and filler/coating recovery would have a substantial impact on the technical and practical feasibility for using paper sludges in other products.

9.1 Material Recovery and Recycling

Sludge Recycling

The most common technique for reclaiming fibre from sludge is to recycle the sludge back into the paper making process. Sludge recycling has been achieved in paperboard (recycled) operations (NCASI, 1993).

Leney et al (1972) initiated studies on the effects of sludge recycling on the properties of corrugating medium. In this study, primary sludges from three mills were added to commercial corrugating medium mixes at levels of 10, 20 and 40% of the mix. Sludge amendments resulted in reductions of flat crush strength, due to the soft chemical fibre in the furnish. It was postulated that had the sludge been added as a substitute for chemical additions, acceptable product qualities could have been attained. The research was not expanded to verify this possibility. It was, however, noted that delamination of the test materials was due to poor bonding, and probably associated with high inorganic filler contents in the sludge amended feedstocks.

Brookover (1977) described and discussed the addition of primary and secondary sludge recycling for paperboard manufacturing. Sludge recycling at this mill involved large quantities of material. The only significant issue was the need to modify the production schedule for various grades of product containing sludge. Adkins (1977) reported on trials directed at the disposal of secondary paper sludge in batch pulping digesters. The sludge additions had no effect on pulp quality; however, the costs associated with additional chemicals and evaporation offset the benefits of this approach. Frederick et al (1981) examined the prospects of using the kraft recovery process as a method for purging non-process chemicals such as Ca, Mg, P, Cl, and Al which were present in secondary sludges. No problems were anticipated with respect to Ca, Mg and P which would leave the system with the dregs. Potential accumulations and fouling associated with Al were identified as the most significant problem.

Sussman et al. (1977), Lavrent'er (1979), Murskaya et al (1979), Monchev (1983), Przybysz et al (1986) and Ignatov and Evelevich (1988) addressed sludge recycling and use for paperboard and bag paper products. For bag paper products poor drainage due to excessive fines were counteracted by the addition of flocculants, and enabled the use of up to 5.8% sludge in the feedstock (mass or volume, unspecified). Ignatov and Evelevich (1988) noted that additions of up to 2.2% waste activated sludge to unbleached kraft pulp resulted in a good quality paper product. In contrast, limited successes were reported by Rosenqvist (1978), NCASI (1979), McAndrew (1985) and Rundell (1985) from the additions of paper sludges to bleached and unbleached products.

Obvious targets for recycling are primary clarifier sludges, and, especially, materials from paper machines, bleach plants, cleaners and refiners before they become contaminated by non-fibrous materials (NCASI, 1993).

Fibre and filler reclamation

The separation and fractionation of fibres and filler contained in effluents and sludges has been examined since the early 1950s (NCASI, 1954). Fibre and filler fractionation has been pursued from non-destructive and destructive perspectives, relative to the organic matter components in sludges. The goal of non-destructive material fractionation is to separate usable paper fibre from other solid materials contained in sludge. Early work was focussed on primary-only sludges, while recent studies have addressed primary and combined primary-secondary sludge matrices, primarily from virgin fibre or first-run recycle papers. Recent work by Maxham (1992b) included the fractionation of secondary fibre and filler substitutes in sludges from deinking operations. The configuration of the reclamation processes and complexities vary depending on the contaminants present in individual sludges. Rosenqvist (1978), McAndrew (1979) and Rundell (1985) noted that process implementation and optimization may involve considerable trial and error approaches.

Fibre recovery. Primary sludges have been the focus of fibre recovery initiatives. In most cases, the approaches to recovering fibres from paper industry sludges involve cleaning and screening processes to separate the usable long fibres from other sludge components. Various system configurations have been employed based on a combination of research and trial and error (Rosenqvist, 1978; McAndrew, 1979; Rundell, 1985). Rundell (1985) noted that the reuse of fibre from virgin fibre sludges resulted in increased pitch deposition on mill equipment. This problem could be overcome by returning the reclaimed fibre to the digester blow tank, where black liquor evidently aids in dissolving the pitch.

Moss and Johnson (1993) described results of trials using a Celleco Hedemora Fibre Recovery System and sludge from the Ponderosa Fibre Products mill, Baltimore. Initial sludge analysis indicated that up to 40% of the sludge matrix consisted of usable fibre (>200 mesh). The system relies on a cleaning stage to remove grit, inks and lightweight contaminants, followed by fibre recovery in a SPRAYDISC filter system. The authors claim good results for both virgin and recycled pulp sludges, although there were no indications of the types of materials to support this claim, other than the work presented in the paper.

Full-scale trials were undertaken at the Ponderosa Fibres mill. Results showed the recovery of 20-22% of the fibre in the sludge, about half of the usable fibre in the sludge matrix. It was evident that additional fibre could have been reclaimed. The operational system at the mill was modified to recover fibre from high-fibre bearing streams before they enter the primary clarifier. It is presumed that this modification was intended to minimize additional sludge cleaning associated with removal of contaminants, grit, dirt and other solids.

Prime Fiber Inc. (PFI) constructed a facility to produce market pulp substitute from waste paper and primary paper sludges, with an operating capacity of 30-50 T/day (Ferguson, 1992). The PFI process involves the separate pulping, cleaning and screening of the waste paper and sludge streams before mixing. The blended pulp is then processed through a deinking system. Maxham (1992a; 1992b) noted that the preferred feedstocks were white paper and primary sludge in which at least 40% of the matrix consisted of reusable fibre. This, in effect, relies on material containing substantial quantities of virgin fibre materials. The 40% recoverable level is the minimum level for economic viability.

Overall economics of the PFI system have been improved by further developments relative to the addition of filler recovery processes (Maxham, 1992a, 1992b), described subsequently.

The NCASI (1993) cited one case in which primary sludge from a non-integrated paper mill was assessed as a feedstock for a deinked tissue mill. The project was ultimately abandoned because of unacceptably high dirt levels which were attributed to the sludge additions.

Filler reclamation. Research on the reclamation of fillers from high-ash (deinking) sludges dates to the early 1950s (NCASI, 1954, cited in NCASI, 1993). These early projects examined the use of calcination to recover the clay fillers for reuse in paper making, filler pigment in rubber products and asphalt. The recovered filler materials were too coarse and abrasive for use in these applications. The problem was attributed to the formation of fused agglomerates during firing in the kiln. By grinding in a ball mill the agglomerations were eliminated. The added costs of grinding and screening exceeded those associated with virgin material (Springer et al, 1977). As such, the project was dropped.

The US EPA (1971) reported results of paper clay recovery by calcination in a rotary kiln. Prior to calcining, the primary sludge was cleaned to remove grit, sand and other solid contaminants before dewatering to 30% total solids. Kiln temperatures were maintained in the range of 830-865°C to avoid the formation of fused particles. The resultant mixed product had a GE brightness of 83-85 and acceptably low abrasiveness. Overall, the recovered pigment was unsuitable for use in paper coating applications. The project was ultimately terminated due to high capital costs for full-scale clay recovery.

ORTECH (1991, confid. client) revisited calcination for the recovery of clays from deinked tissue mill sludge. The sludge had a consistency of 30% total solids after dewatering, and contained 40-60% ash on a day-to-day basis. Under laboratory conditions, the dewatered sludge was calcined on a batch basis in a ceramics kiln at temperatures ranging from 0-1200°C.

At temperatures <800°C, the recovered clays possessed a low brightness (50-53), but, otherwise, consisted of fine powder without agglomerations. For temperatures >800°C, the recovered material had a low brightness (55-60), powder consistency and suitable textural properties for paper making. The best overall results with respect to brightness (81-83) were obtained for material fired at 800°C. Analysis of calcined material, by x-ray diffraction revealed that up to 30% of the matrix in individual samples consisted of amorphous crystalline materials. Mineralogical analysis indicated that >20% of the matrix consisted of calcium oxides.

The client had no in-plant uses for the recovered clay material, and the costs associated with a full-scale rotary kiln were deemed to be prohibitive. Searches for external users - ceramics/refractories and metallurgy produced minimal results. Operations using virgin clays were unwilling to risk contamination of products containing the sludge filler. Moreover, none of the operations contacted had sufficient capacity to store and process 60 T/day of the sludge, in addition to normal virgin feedstocks. The project did not advance beyond the laboratory scale studies.

Wet air oxidation (WAO) technology has received considerable attention for mill effluent and sludge treatment. The WAO process was conceived in the mid-to late 1800s, and was first applied to the treatment of pulp and paper effluents in 1912 (Ontario Research Foundation, 1976). Prominent uses of WAO include the treatment of black liquor and recovery of pulping chemicals (Cadotte et al, 1976; Ellis and Fenchel, 1980; List 1982). Full-scale WAO systems operate at one large U.S. mill, Repap, Wisconsin, and at the Papierfabrik Biberist mill, Switzerland. The latter operation, described by Ellis and Fenchel (1980), uses this technology specifically for the recovery of filler clays for in-mill uses. Previous work by Flynn (1976), Springer et al. (1977), Cadotte and Cobb (1978) and Maxham (1992b) addressed the application of WAO for filler recovery, including properties of reclaimed material.

Wet air oxidation involves three competing chemical reactions under high temperature (375°C) and pressure: heterogeneous (solid surface) oxidation; hydrolysis; and liquid-phase oxidation. The three reactions result in the oxidation of organic macromolecules forming the cellulosic solids to CO_2 and H_2O, and low molecular weight carboxylic acids (e.g. acetic acid). Most of the organic material entering a WAO process, including paper sludges, is eliminated by oxidation. The temperatures involved in the process are substantially lower than for calcination, and, as a consequence, WAO processes do not result in unacceptable alterations to the calcium carbonate and titanium dioxide contents (Ellis and Fenchel, 1980).

Sludges must be cleaned and screened to remove coarse materials that would cause fouling of the WAO system. Typically, the sludges are added to the process as an aqueous slurry (<10% total solids), and, at the end of the process, the liquid and solid phases are separated. The liquid phase is usually discharged to the effluent treatment plant, while the recovered solids can be cleaned and screened before reusing.

Experiments completed by Cadotte and Cobb (1978) and Robey and Laughlin (1981) produced reclaimed filler with unacceptably low brightness (50-58). The poor quality coupled with anticipated high costs for full-scale operations resulted in suspension of further work. Springer et al (1977) reported that WAO reclaimed fillers possessed acceptable properties for use other than low brightness. Brightness could be improved to some degree by blending with virgin material. It was also suggested that oxidative bleaching would improve brightness. On the positive side, paper produced with reclaimed material resulted in a higher degree of opacity, with good printing qualities.

In spite of the promising experimental results, WAO processes have not gained widespread acceptance. Reasons for this can be attributed to high capital costs for a system that would be adjunct to primary and secondary treatment systems. Accumulation of calcium sulfate and calcium oxalate scale on heat exchangers was identified as a problem. Scale build-up requires frequent boil-out of the system using nitric acid. Corrosion problems associated with the processing of chemical pulp liquors and effluents have also been indicated (ORTECH, 1993; confid. client). Low brightness was linked to iron in mill wastewaters (NCASI, 1993).

Shaefer (1992 - cited in NCASI, 1993) indicated that the capital and operating costs for WAO processing of 30 T/day of sludge was about $200/T, including credit for the reclaimed filler.

Springer et al. (1977) completed an experimental program to evaluate potential filler recovery by foam flotation, centricleaning, screening and wet air oxidation. Only the latter two were deemed to be feasible. Screening using a Sweco vibrating screen enabled recovery of about 70% of the filler contained in the sludges tested. Fillers recovered by screening were of acceptable quality with the exception of low brightness. Fine fibres incorporated with the clay fractions did not have an adverse effect on paper and printing quality. Oxidative bleaching processes would probably improve brightness.

The PFI system described by Maxham (1992a, 1992b) relies on cleaning and screening processes to recover usable fibre and filler material as indicated previously. For deinked secondary fibre sludges, intermediate steps are required to remove the fine ink solids from the matrix. Ink removal was accomplished by adding chemicals which promote the aggregation of ink solids for separation. It was found that a suitable brightness could be accomplished both for screened and WAO reclaimed fillers by bleaching chemicals. However, it was noted that the sequence of bleaching was critical, as some chemicals can result in colour fixing that cannot be reversed. Maxham (1992b) showed that the recovered fine fibre-filler material was suitable for reuse as paper filler but not for coating pigment. As a filler additive, the recovery is economical and cost competitive with virgin materials.

9.2 Manufactured Product and Commercial Applications

Options for using paper industry sludges in manufactured products have been grouped into the following four categories:

1. Building products and ceramic applications
2. Biofuels and fermentation products
3. Animal feed and food applications
4. Miscellaneous product applications

In addition to these sludge use categories, the NCASI (1993) and Wiegand and Unwin (1994) addressed gasification and pyrolysis technologies; sludge pelletization for fuel; supercritical water extraction; landfill barrier or capping applications; and pet litters. These areas have been deliberately excluded from this report.

Although gasification and pyrolysis technologies have been well established for over a century, and are now being assessed for the processing of organic waste materials, there is little technical information or experience specific to paper industry sludges (NCASI, 1993). By-product gases and organic/hydrocarbon-like materials produced during pyrolysis have fuel value. However, in many cases, the fuel by-products are recycled within the system, and, thus, pyrolysis really constitutes a disposal technology.

The NCASI (1993) addressed the pelletization of sludges as a use option. The most prominent examples involve the production of sludge pellets for use as a fuel. Discussion of sludge fuel pellets has been excluded, due to the association with incineration. However, references to pelletized sludge use in building products and agricultural applications (carriers for pesticides and nutrients) were examined.

Supercritical water extraction, or otherwise known as supercritical fluid extraction technologies, has not been extensively tested for the treatment/processing of paper industry sludges. The process is similar to WAO but operates under higher temperatures (>375°C, the critical temperature for water) and pressures.

Landfill barrier and capping applications of paper industry sludges have merit, but involve landfill disposal. In one case, an application was made for approval of paper sludge as a landfill capping and daily cover material. The status of this project is unknown.

The use of paper industry sludges in pet litter formulations has achieved some commercial success. The market for these products is highly competitive, and based primarily on low cost virgin clay mineral materials. It is doubtful, based on experience, that paper sludges will be used extensively in pet litters. Finally, the use of paper sludges in pet litters essentially involves the transfer of one disposal problem (sludge) to another (pet litter).

Building products and ceramic applications

The use of solid wastes and sludges in building products has been extensively examined. Within the last decade, studies have assessed the potential use of waste glass, wood fibre, foundry sands and sludges in concrete, bricks and ceramics, asphalt and composites. In many cases these product lines could be viewed as ideal repositories for waste materials.

Utilization of paper industry sludges in building products is highly attractive, because the quantities of material involved, and product markets are of sufficient scale to handle sludges from one or two mills (NCASI, 1993). Moreover, these product applications require minimal pre-treatment or processing of sludge before use.

Sludge utilization in cementitious materials and ceramics has been accomplished in three general ways, as follows:

1. Incorporation of sludge as a feedstock in the production of cement, for example, cement kilns
2. Direct incorporation of whole sludge in the product mixture such as concrete
3. Production of a by-product or additive such as light-weight aggregate (LWA).

- **Cement production**

The use of high-ash content paper sludges as cement kiln feedstocks has been addressed by several companies (NCASI, 1993). Basic raw materials for conventional Portland cement include: limestone (calcium carbonate), clay and silica, and may also include aluminum and iron. High-ash sludges from fine paper and deinking operations are potential candidates for use in cement production due to the clay and chemical contents. Table 6 presents a comparative summary of chemical data for Portland cement, boiler ash and sludge from a deinked fine paper and deinked tissue operations. The data on cement, boiler ash and deinked fine paper were obtained from Huston (1992). Data on the deinked tissue sludge was derived from the chemical analysis of calcined material (ORTECH, 1990, confid. client). The paper sludge samples yield higher SiO_2 and AlO contents relative to the Portland cement sample, and lower levels of FeO, CaO and MgO.

Huston (1992) indicated that the proponent mill transferred all of its primary sludge and boiler ash to the cement plant (60 and 50 T/day respectively), which accounted for about 2.0% of the total cement kiln feedstock.

The sludge is mechanically dewatered to 55% total solids and subsequently dried to 85-95% total solids in a rotary kiln. Initial concerns for strong odours and the blinding of cement screens were resolved by drying the sludge to 85-95% solids, and adding the material to the feedstock after screening. Huston (1992) indicated that the costs of the process to the mill were in the range of $30-35/T (1992-US Dollars).

Buchinger and Ernstbrunner (1991) describe the process whereby deinked secondary fibre sludge from a tissue mill is dewatered and subsequently transferred to a nearby cement company. Sludge is processed in a kiln with other cement feedstocks to yield a suitable cement product. The process has operated successfully and economically, according to the authors, although no details were provided.

For high-ash sludges, cement production is attractive, although there are few data available to evaluate process feasibility, product qualities and performance in various product formulations.

TABLE 6: COMPARATIVE COMPOSITIONAL DATA FOR PORTLAND CEMENT, PAPER SLUDGE AND BOILER ASH.

(from Huston et al., 1992)
Data expressed as precent dry solids

Material	SiO	AlO	FeO	CaO	MgO
Cement	20.9	5.2	2.3	64.0	2.8
Sludge	27.0	20.0	0.6	19.0	0.8
Coal fly ash	37.0	17.0	3.4	1.3	0.6
Deink sludge*	32.6-33.0	27.1-27.5	0.39-0.4	24.7-25.3	1.43-1.50

* 100 % deinked secondary fibre sludge for tissue production (ORTECH, 1991, confid. cleint)

- **Sludge use in cementitious composites**

The use of organic materials and fibres in reinforced cementitious composites has gained acceptance. Organic fibres from green plants have been used extensively for reinforcement in developing nations (Thomas et al, 1987). Wood pulp is being used in Australia for cementitious composites (Coutts and Knightly, 1982; FIP, 1985). Harper (1982) addressed the use of clean paper pulp as a substitute for asbestos fibre. Wood-based pulp based composites are less costly to produce when compared with manufactured glass fibres. Organic fibre additions to cement and concrete improve product durability and pumpability, and reduce cracking due to shrinkage (Nutt, 1973; Razl, 1985).

Whereas high-ash sludges are appropriate feedstocks for cement production, high-fibre (sulfite, groundwood and thermomechanical) sludges would be most appropriate for cementitious composite applications.

Alkire and Newton (1975) examined the effects of adding sludge from a groundwood-kraft process to a cement mortar mixture. The sludge contained 80% organic matter. Experimental conditions defined by the authors involved the drying of sludge at 105°C, grinding and screening (100 mesh). The dry screened sludge was combined in varying proportions with Ottawa sand and dry cement. Water was added to the cement mixtures and allowed to cure before testing, according to ASTM procedures. Samples of the various mixtures were tested to determine compressive strength for 1, 7, 14 and 28 day curing periods. For sample mixtures containing up to 0.5% sludge, compressive strengths were similar to those obtained from conventional cement samples as controls. As the sludge content increased above 0.5%, compressive strength decreased. No interpretation, or analysis, was provided to address the implications of these results relative to full-scale applications.

Subsequent research reported by Thomas et al (1987) addressed the addition of deinked secondary fibre sludges to concrete formulations. The study showed that paper sludge-cementitious composite materials could be used economically in building blocks, wallboard and paneling, shingles, fire retardants or fire proof materials. Beyond the product applications, the study examined processing techniques for wet (raw undewatered sludges - 3-6% total solids), and dewatered (25-40% total solids) material.

Based on experience, dewatered paper sludges can have variable physical qualities. For instance, sludges dewatered to 15% total solids behave as thick slurries, similar to poured concrete, and, due to adhesion, these materials are difficult to mix. When dewatered to 30-40% total solids, paper sludge consistency may vary from pea-stone sized (0.5-1.0 cm) agglomerations to "curled" sheet structures. Rewetting and dispersion of agglomerated solids is difficult. Thomas et al (1987) documented similar problems on mixing dewatered sludge with cement.

At consistencies >40% total solids, dewatered sludges may vary from loose and light fibrous material resembling fibre insulation to hard, brittle agglomerations or sheets. The dry agglomerations and sheets would require shredding in a hammermill to reduce the masses to loose fibres, to enable mixing. Dry fibre solids are difficult to rewet, and, in dilute slurries, the dry fibrous materials tend to separate and float on the surface. Separation of solids, as such ,would result in compositional heterogeneities of the concrete-sludge mixtures. Thomas et al (1987) found that better mixtures were obtained using raw undewatered sludge. Decanting was required to remove the excess water from the mixtures.

Odour problems and related bacteriological effects on the pH of the sludge material were identified as potential problems relative to dewatered sludges. It was surmised that the level of bacterial activity and, hence, odour generation and fibre decomposition ,would be minimized under raw undewatered sludge conditions.

Thomas et al. (1987) stated that their research was based on short-term tests, and, due to unsatisfactory results and experience with other organic fibres, longer-term studies were required to determine durability and dimensional stability of composite materials.

Other research projects cited in NCASI (1993) indicated good performance results for mixtures of Portland cement, coal fly ash, sand and sludge. However, long-term data and analysis were not available.

- **Lightweight aggregate**

Aggregate refers to materials used as fillers in various construction applications. These materials include crushed stone, and various grades of granular materials used in concrete, masonry, building blocks, asphalt and fill for road beds. Light weight aggregates are used to produce composites which possess acceptable strength properties but with substantially reduced bulk density. Shale, clay and slate have been the traditional light weight aggregate components used (NCASI, 1993).

The use of municipal sludge ash as a light weight aggregate has been addressed (Tay et al, 1989). However, there is limited experience with respect to the use of paper industry sludges. The NCASI (1993) cited one example in which paper mill sludge was combined with other wastes to produce a light weight aggregate. According to the authors, the paper mill sludges do not have sufficient fusible matter to yield strong ceramic pellets, and, therefore, require blending with other feedstocks. Pilot trials resulted in 20 t of product for test marketing. Encouraging results led to plans to produce 250 t/day of light weight aggregate from 700 wet t/day of paper sludge, and 125 t/day of boiler ash.

Ceramic applications

The potential use of paper industry sludges in ceramic products, including bricks, was indicated in previous citations. Prouty (1982) addressed the possibility of adding municipal sludges, and possibly pulp and paper sludges, to brick making feedstocks. Organic amended brick and ceramic mixtures are lighter in weight, possess higher absorptive and porosity properties, and higher insulating values when compared with conventional clay brick mixtures (Liebig, 1977; Prouty, 1982).

The basic raw materials for brick making include clays which possess a high degree of plasticity (e.g. smectites, illites and chlorites, Grim, 1962). Generally, the clays and other feedstocks are blended in a dry state prior to the addition of water. Stiff-mud mixtures involve water contents of 12-15% (weight basis), and 20-30% for soft-mud mixes. The wet clay mixture is moulded and/or cut, and then dried in kilns at temperatures of 30-200°C for varying periods. The dried brick or ceramic units are then fired in a kiln according to a regulated temperature gradient from 0-1200°C, and then allowed to gradually cool. Gradual cooling is required to prevent cracking of the product. Under field conditions, dry sludge additions of up to 50% have produced acceptable product qualities.

The patent assignment of Liebig (1977) represents the only specific case using paper mill sludge as a feedstock component. In this case, the results indicated a suitable light weight brick product, with respect to quality and performance.

Overall, the experience and data on the potential uses of paper industry sludges in ceramic applications are limited, based on available literature. Intuitively, marketing this application of paper sludges will be difficult outside of the major brick producing areas of Southern Ontario. Prior experience with whole sludge and calcined materials produced minimal interest in handling and processing paper industry sludges (ORTECH, 1990, confid. client).

Gypsum board composites

Hamilton (1991) suggested that paper industry sludges could be employed in the production of fibre filled or gypsum board composites. Thomas et al (1987) also identified potential uses of paper sludges in composites that would be used for paneling, but did not explicitly assess gypsum board products. Preliminary assessments under laboratory conditions showed that the addition of deinked tissue sludge to conventional mixtures resulted in acceptable gypsum board composites (ORTECH, 1990, confid. client). The laboratory studies were abandoned for the following reasons:

- Industry competitiveness, and concerns for substitution of virgin or recycled gypsum in new products
- Uncertainty with respect to formulation and product performance relative to conventional materials
- Industry imposed limits of 2.0% total fibre (paper) content in board products using recycled gypsum
- Abundant supplies of recycled gypsum and virgin material
- Anticipated supplies of by-product gypsum from flue gas desulfurization from Ontario Hydro and other facilities.

The economics of transferring sludge from individual mills to gypsum board producers probably discourage this option due to location and/or distance.

Biofuels and Fermentation Products

The biological conversion of cellulosic matter to fuel additives and food related products has received some attention. The principal areas of research, relevant to the utilization of paper industry sludges include:

1. Ethanol production as a fuel
2. Protein recovery

- **Ethanol production**

Ethanol is currently produced as an additive to gasoline for automobiles. The principal sources of ethanol have been cane syrup and starch contained in various plants (Lynd et al, 1981; Aterthun and Ingram, 1989). These specific high quality feedstocks are expensive, and also represent a small fraction of the total carbohydrate content of plants. Lower cost sources of carbohydrates, including cellulosic materials, have been sought, including: plant leaves, stem/stock, cobs, hulls and so on. Municipal wastes and paper industry sludges represent significant low cost sources of cellulosic matter (Choudhury et al, 1993; NCASI, 1993; Swann, 1993).

Saccharomyces cerevisiae or Zymomonas mobilis are largely responsible for ethanol production involving cane syrup, corn starch and other sugars (Alterthun and Ingram, 1989). The crystalline and polymeric structure of cellulose (carbohydrates) are resistant to microbial attack, and require enzyme attack or hydrolysis to reduce the material to usable sugars. No organism has been found, in nature, which can rapidly and efficiently metabolize the different sugars in plant matter into ethanol or any other valuable product (Alterthun and Ingram, 1989).

Escherichia coli has been shown to metabolize all major sugars contained in plant biomass. Ingram and Conway (1988) and Aterthum and Ingram (1989) described a technique for genetically altering E. coli to produce ethanol from cellulose and hemicellulose. In essence, the recombinant E. coli, containing genes from Z. mobilis, encoded for the ethanol pathway, were effective in producing ethanol from cellulose. Ethanol yields from the recombinant E. coli were higher relative to those for S. cerevisiae with glucose.

The research of Ingram and Conway (1988) and Alterthun and Ingram (1989) did not address ethanol production from paper industry sludges, specifically. Low-lignin content paper mill sludges, from primary clarifiers would represent candidate materials for evaluation. Due to the higher degree of delignification achieved during chemical (sulfite and kraft) pulping relative to groundwood and other mechanical processes, sludges from these operations would be candidates for research. The higher lignin content in groundwood/mechanically pulped materials would inhibit microbial action and, hence, fermentation.

Ethanol production yields effluent which must be treated, and, therefore, this technology will not eliminate effluent nor sludge output. Undigested solids (cellulosic) and biomass comprise the major solid constituents in the effluents from fermentation. Yield, effluent quantity and sludge outputs from ethanol production based on cellulosic matter, other than corn, has not been explicitly defined.

It remains to be determined whether or not ethanol production can be adopted for the full-scale processing of paper industry sludges. It is, however, evident that these process do not involve secondary sludges.

- **Protein recovery**

Apart from ethanol production, the second major biological conversion or fermentation application involves the recovery or production of protein for livestock feed and/or food. Turnbull (1982), Harkin and Crawford (1983) and Young (1984) described the conversion of cellulosic matter to usable protein.

Various fungi play a dominant role in the decomposition of cellulose, and include thermopilic types or species (Alexander, 1977).

Thermomonospora fusca is a strongly cellulolytic, thermophillic filementous actinomycete that grows readily on low-lignin cellulosic materials. Thermophillic decomposition by this organism results in substantial reductions in waste volume and high yields of protein that can be used for livestock feed (Harkin and Crawford, 1973). The extra-cellular polysaccharide enzymes contained in the spent fermentation broth could be used in foodstuff and beverage industries.

The patent claim filed by Young (1984) indicated that a protein-enriched product was obtained from the conversion of cellulosic materials by the fungus Chaetomium cellulolyticum. The patent further claims that the bioconversion process would be applicable to various cellulose bearing materials including pulp mill sludges. However, none of the experimental data presented in the claim included pulp or paper mill sludge as a test example.

Livestock feed

The potential use of pulp and paper sludges as livestock feed has received attention since the early 1970s at least. Currently there are no commercial operations employing paper sludge as feed.

Low ash-content primary and secondary sludges were viewed as candidate sources of livestock feed (Harkin, 1982; Rogers, 1982). High ash-content sludges were deemed to be undesirable due to the intrinsic quantities of inorganic matter, which have no food value, and add bulk only (Harkin, 1982).

ITT Rayonier implemented studies to determine the feasibility of using secondary mill sludge rich in organic matter, nutrients and protein, as a commercial feed product. The results were favourable and resulted in commercial operations. However, the NCASI (1993) reported that this operation was abandoned due to the lack of market acceptance, and poor palatability.

Other paper sludge uses

The foregoing sections addressed the major potential uses for paper industry sludges in commercial product applications. Abstracts, patent claims and secondary literature sources identified a number of other prospects that warrant description. Detailed assessment of these documents was not possible due to limited access and the abbreviated state of abstracted work.

• Sludge pelletization

The NCASI (1993) included a major section on the pelletization of paper industry sludges. The principal applications discussed in the report were mass and volume reduction, and the production of pellets for fuel. Shitano (1983) described the production of waterproof pellets, from dried paper sludges, for use in building insulation. The NCASI (1993) identified proprietary applications of pelletized paper sludge as carriers for pesticides and other agricultural chemicals. The patent claim by Neckermann and Wooding (1982) described the conversion of sludge to lipophilic granules by heating to 162°C (350°F), milling and forcing through a screen. The resultant soft product would be suitable for use as insulating material.

- **Moulded fibre and fibre board products**

Damhaug (1978) summarized experiments and full-scale experience on the production of moulded packaging products for produce and other food applications. The feedstock consisted of newsprint sludge, without deinking, and waste paperboard. The sludge (primary) additions amounted to 10-15% of the total pulp feedstock.

Emery (1994) provided a technical overview on the use of proprietary technology for the manufacture of moulded packaging using paper sludge and/or other high fibre streams. Fibre obtained directly from the paper machine or primary sludge could be used.

The production of moulded packaging from sludges is viable. However, there is a need for research on regulatory policy for product lines which contact food and beverage products. Rigorous testing requirements for leachable chemical contaminants from recycled paper materials were stipulated by the Health Protection Branch, Health and Welfare Canada (ORTECH, 1992, confid. client). Testing and monitoring requirements were required for a period before approvals for use would be granted.

Roland and Helge (1977) described the production of fibre board from pulp and paper sludge, although details on the approach and results were not available at the time of writing.

Nakajima et al (1982) described the addition of paper sludge, predominantly as short-fibres, to starch, alum and a cationic polymer to produce fibre board suitable for use in furniture and building materials.

Bukhteev et al (1984) filed a patent claim on the processing of activated (secondary) sludge in a kraft process. The alkaline pulping process destroyed the biological component. Resultant pulp was used for the production of cardboard and fibre board products.

Chernousev (1983) described the manufacture of paperboard containing up to 15% activated sludge biomass. The product was used in one of the board base layers.

The process patent assigned to Grudinin et al (1984) involved the treatment of pulp and paper mill sludges, including secondary sludge with alkali and then dewatering. The filtrate was used in the white water formulation, while the dewatered solids were recovered to make fibre board and paperboard.

Haataja and Lund (1980, 1981) described patented formulations for the production of moulded, one piece pallets. Dried pulp and paper mill sludge was blended with fibrous reinforcing material (bark), and a resinous particle board adhesive.

Pridham and Cline (1988) noted that feasibility studies were undertaken relative to the manufacture of biodegradable plant pots, for horticultural use, from combined primary and secondary sludge. The sludge material was derived from chemical sulfite-deinking operations. The project was dropped due to excessive capital and operating costs.

Hamilton et al. (1991) provided a general discussion on the manufacture of composites, fibre board and other products from fibrous materials. Although reference was made to the potential use of paper industry sludges no specific examples were provided.

- **Resinous fibre applications**

Hearon and Lamberth (1975a, 1975b) described the formulation of resinous materials consisting of phenolic and amino thermoset resins and paper sludge, mixed on a 2:1 basis (resin:sludge). The application is ideal for short-fibre content, but not long-fibre materials. In this application, sludge serves as an extender or filler and can be used in the manufacture of particle board, plywood and glue-lam lumber products.

The patent claim by Bertelloni (1982) addresses formulations involving paper industry sludge and other additives such as resins and clays for the production of coatings, insulation and packing materials.

- **Miscellaneous applications**

Ando (1979) developed a formulation consisting of asphalt emulsifier added to vigorously stirred sludge and subsequent moulding. The resultant product is water resistant and flame resistant and deemed to be suitable for use in roofing materials, outer wall and sound insulation products.

The Japanese patent assigned to Tokai Pulp (1979) described the combined addition of alum sludge with paper mill sludge, synthetic and wood fibre to clay. The resultant product was suitable for use as wall plaster and tile.

Masuda (1976) and Jousimaa (1978) described the drying of paper sludge to <5.0% moisture, granulation and mixing with thermoplastic pellets. These fibre plastic composites possessed higher strength and hardness relative to the controls.

Secondary sludge utilization

A number of reports cited previously described experience with the utilization or processing of combined primary and secondary sludge or secondary sludge in paperboard manufacture, and the essential destruction of secondary sludge in kraft pulping, or chemical recovery processes (pp 59-60). Overall, the prospects for utilizing secondary sludge alone have not been extensively examined.

There is a need to examine and develop strategies for the handling of secondary sludges, perhaps based on the experience gained from the treatment of municipal sewage, and municipal sludge handling. Because secondary sludges are dominated by biomass and associated colloidal matter, and may not be amenable for use in cementitious materials, or material recovery applications, there is a need to develop strategies for using secondary sludges alone. Due to the high nutrient content of secondary sludges, land application and agricultural/silvicultural product applications would be attractive options for their use.

10. MARKET AND ECONOMIC CONSIDERATIONS

The purpose of this section is two-fold:

(a) To synthesize and combine available information on potential sludge uses relative to mill and/or sludge types

(b) To define and review the market uses that have had a major influence on the commercial uses of paper industry sludges.

These two purposes are interrelated. It is necessary to match the general and mill specific sludge properties and types to prospective uses, and, second, to define the market issues or constraints based on economics, manufacturing requirements and capacity and location.

10.1 Summary of Potential Paper Sludge Uses

Previous sections of this report identified the major manufacturing and effluent treatment processes at pulp and paper mills; sludge composition; and a broad range of potential sludge uses. To facilitate further focussed assessment and commercial developments, potential sludge uses have been grouped relative to the mill and sludge types in Table 7.

The groupings presented in Table 7 are based on the following assumptions:

(a) Individual mill sludges are derived from primary only, or combined primary and secondary treatment processes

(b) All effluents from mill sources are combined for treatment in one system

(c) Sludge utilization is based on "as-received" sludge, either raw or dewatered

Table 7: Summary of mill types and potential sludge uses

Mill Type		Product lines	Sludge properties	Potential uses
Integrated				
	Groundwood Kraft Sulfite TMP NSSC	newsprint packaging board tissue	high fibre and low ash primary only combined primary and secondary	fibre recovery cementitious composites fibre composites fermentation products
	Groundwood Kraft Sulfite TMP	writing papers bond ledger magazine	1:1 fibre to ash high ash	fibre and filler recovery cementitious composites cement light weight aggregate
	Recycled paper board	linerboard match stock construction papers	high fibre, low ash.	fibre recovery cementitious composites fibre composites fermentation products
	Deinking	newsprint tissue	high fibre, low ash high ink solids	fibre and filler recovery cementitious products fibre composites cement
	Deinking	fine papers bond ledger	1:1 fibre to ash	fibre and filler recovery cementitious materials cement fibre/filler composites
Non-integrated				
		Fine papers bond ledger specialty papers	1:1 fibre to ash	fibre and filler recovery cementitious materials cement fibre/filler composites
		tissue wadding	high fibre	fibre recovery cementitious composites fibre composites

In the first case, the bulk of the fibrous and inorganic matter (fillers and coatings) are associated with primary clarification. Due to the addition of secondary treatment systems at a number of mills, resultant sludges would be comprised of primary and secondary solids to varying degrees.

Second, with one exception, mills in Ontario rely on a single treatment system for all mill effluents. The one exception includes a separate primary clarification system for wet debarking effluent treatment. Changes to the configuration of effluent streams and treatment systems to accommodate sludge uses, for instance the separation of deinking streams from other effluent sources, could be possible if it does not add to the capital, operating and maintenance costs.

Third, raw sludges have a consistency of 3-5% total solids. Dewatering to 30-50% total solids has been the common practice to enable landfill disposal and land application. It is evident that raw sludge is better suited for use in some cementitious materials or composites (Thomas et al, 1987). Also, raw sludges would be more appropriate for fibre recovery processes (Maxham, 1992b), to prevent fibre damage due to imbedding of inorganic solids. If wet air oxidation processes are employed for clay recovery, raw sludge (<10% total solids) would be appropriate, while dry sludge, >40% total solids, would be appropriate for calcination and cement kiln applications.

Many of the integrated pulp and paper mills in Ontario use combinations of different pulping processes (Table 2), such as kraft and groundwood, sulfite and groundwood, and TMP-groundwood-deinking. It is, therefore, difficult to categorize a sludge as being unique to kraft, sulfite, groundwood or other mechanical pulp and paper production.

In general, fibre-rich sludges would be amenable to fibre recovery, and use in fibre or cementitious composites. Fermentation and biofuel applications would also be suited to high-fibre content sludges. High-ash content sludges from the production of fine papers, ledger and bond, and some deinking operations would be suitable for fibre and filler recovery, and use in various cementitious materials.

Sludges from the deinking of old newspapers and magazines tend to possess high degrees of colour (dark blue to black) due to the carbon black inks, and pigments. Removal of the inks and pigments from the sludge could be difficult, and, thus, efforts to recover fibre should focus on the white water off the paper machine, and other effluents excluding the deinking stream. However, data from one operation indicated that effluent from deinking processes accounted for almost 50% of the suspended solids loadings to the primary clarifier. If usable fibre yields from effluents and sludges are <40%, fibre recovery is not feasible (Maxham, 1992b).

Bench-scale trials based on a combined primary and secondary sludge from one deinking operation showed that fibre (>140 mesh) could be recovered, but with a high degree of contamination from flecks of ink. Due to contamination by ink solids, the recovered fibre could be used in low grade board or perhaps some fibre composites as a filler or extender (ORTECH, unpub. internal study, 1995). Odour and other problems associated with secondary sludge solids were overcome by washing, screening and treatment with a sodium hypochlorite solution. Further experimental work in this area could lead to a commercial, albeit low grade, fibre pulp.

The effect of secondary sludge components on storage and potential uses warrants further substantial research. If combined primary and secondary sludges are stockpiled prior to use, biological activity could result in decomposition of the cellulosic matter, and formation of partially humified organic materials. For some applications, sludge decomposition could adversely affect the properties and performance of products including, cementitious composites, fibre composites. Thomas et al (1987) noted that the alkaline pH of cementitious materials may be sufficient to inactivate or sterilize secondary sludge components. However, long-term stability and performance testing is needed before considering the use of combined primary and secondary sludges in building products.

Market and Economic Constraints

In spite of the research and development activity since the early 1950s, the number of commercial scale uses of paper sludge is limited. The most prominent commercial applications have involved the following:

1. Direct sludge recycling in paper product manufacture
2. Lime kiln production of cement
3. Light-weight brick
4. Market pulp substitute and by-product filler materials
5. Livestock feed

Harkin (1982), and the NCASI (1993) report attributed the lack of commercial success to variable and, often, inconsistent properties of paper industry sludges, excessive capital and operating costs for alternative sludge uses and product lines.

Interestingly, the few commercial successes essentially involve whole sludge, and require minimal modifications to mill processes for the separation/fractionation of sludge components. It is prudent to note that the PFI operations rely on whole sludge feedstocks, which are fractionated to produce market pulp substitute and by-product fillers, that are economically competitive. With a production capacity of 30-50 T/day, the PFI operations are quite small when compared with the integrated pulp and paper mills in Ontario which may generate 100-200 T/day of sludge. However, due to the initial success demonstrated by PFI, and planned expansion, fibre and filler recovery represents an attractive area for sludge management. Moreover, due to current shortages of good quality waste paper, increasing emphasis may be placed on improved fibre and filler recovery, in the near future.

Other commercial successes appear to be linked to the proximity of individual mills relative to manufacturing facilities and markets. Examples of concrete or cement production from paper industry sludges involve manufacturing facilities that are in close proximity to paper mills. Although little information is available on markets, it is presumed that cementitious products containing paper sludges are used locally.

It was evident from the literature that the bulk of the research and development activity associated with paper industry sludge use has been supported or undertaken by the paper products industry. Limited involvement and interaction between the paper industry and off-site manufacturers may have adversely affected commercial development.

Resistance to the use of sludges and other wastes in commercial products may be attributed to public perception and attitude. Until recently, for example, the new home-buyer preferred the use of new or virgin materials in home construction, a factor which would have precluded waste or by-product use in building products. The development of "green industries" and programs such as Build Green have helped to overcome the perceived problems of using waste materials in new products. Linkages between the pulp and paper industry and Build Green or other 3Rs initiatives could assist in developing and marketing products containing paper sludges.

The concerns for sludge management are not confined to single mills, but, because paper industry sludges differ compositionally on a mill-by-mill basis, potential commercial uses for paper sludges must consider individual mills, local market prospects, manufacturing capacities and capabilities, and regional or larger-scale markets. Mills situated in the highly populated areas of southern Ontario have access to various manufacturing facilities, e.g. cement/concrete plants within short distances of individual mills.

There are, however, major economic issues that require further assessment. For instance, relatively small non-integrated mills in the Toronto and Niagara areas have limited available space on-site, and relative to adjacent properties, to enable the development of manufacturing facilities using sludges. Dewatered sludges (30-40% total solids) can be transported economically within about 40-50 km of the mill source, based on experience with land application programs. For some uses, including fibre and filler recovery, and cementitious composites, raw undewatered sludges (3-5% total solids) are preferable. For raw sludges, substantially greater volumes of material must be transported or transferred to manufacturing sites, e.g. 70 dry T/day of sludge amounts to 200 T/day with 35% total solids, and 1,750 T/day with a consistency of 4.0% total solids. From an economic perspective, the implications are significant, based on sludge haulage costs. In this regard, sludge with a consistency of 35% total solids is hauled to farm sites, in the Niagara region, for example, at a conservative cost estimate of $10/T or $2,000/day (200 T/day of sludge). Using this cost estimate for raw sludge, for alternative uses, the haulage cost alone would amount to $17,500/day, or $6.13 M/year for a 350 day production schedule. The costs, alone, of hauling raw sludge to an off-site manufacturer are prohibitive, unless there are arrangements for cost-sharing or compensation of some form.

Recent market pulp values are in the range of about $600/T, while filler grade clays are valued at about $200/T (U.S.) (Maxham, 1992b). The economic analysis presented by Maxham (1992b) allowed for a tip fee of $187/T (U.S.) of waste paper or sludge, applied by PFI. Municipal landfill tip fees in southern Ontario are <$100/T. Small non-integrated mills with limited on-site space would have to rely on off-site facilities for the recovery of fibre and filler materials. If a tip fee is applied, and exceeds $10-20/T, off-site fibre and filler recovery would probably not be adopted. In contrast, large integrated pulp and paper mills could benefit from on-site fibre and filler recovery, depending on capital, operating and maintenance costs, relative to economic returns from material recovery.

Northern Ontario mills, situated in small communities may represent the single major industrial or commercial enterprise. Establishing large-scale manufacturing plants in small northern communities may have to depend on larger markets, outside the region. Due to distance and transport costs, high value products would have to be produced. Manufacturing at remote locations would be discouraged by similar competing products derived from sludges, in the principal market areas such as southern Ontario.

Very few market and related economic data are available to assess the process and product viability relative to the use of paper industry sludges, especially for mills situated in Ontario. Although various alternative uses for paper industry sludges may be technically possible, substantial economic and market related assessments are required to establish the practical feasibility of sludge use for individual mills and their respective locations.

A survey of building product manufacturers (concrete, cement, ceramics and refractories) conducted in 1990 (ORTECH, confid. client) produced variable, and, generally, negative results relative to paper sludge use. This survey was applied to manufacturing operations within the urban area from Oshawa to Niagara only, and may not reflect conditions or responses for other areas. Reasons for not considering paper industry sludge as a feedstock are summarized as follows:

1. For use in cement and concrete, sludge was viewed as a nuisance. Although dewatered sludge (35% total solids) contained up to 50% ash, the yield as ash would only have been 10-20 T/day, and <2.0% of daily production.

2. For concrete, the major concern was the need to reformulate mixes to accommodate sludge with few data on product performance, and the prospect of developing new product lines with undefined market prospects. Use of paper sludges would have been considered if appropriate formulation and product performance data were available. Specific concerns included the need for long-term stability and performance testing to minimize product liabilities.

3. Lack of on-site facilities to store and process wet sludge, especially biologically active material, e.g. secondary sludge.

4. Lack of leachate collection or control capabilities, and concerns for odour problems from biologically active sludge. Substantial concerns were expressed for the capital, operating and maintenance costs associated with special leachate and effluent treatment facilities, for raw sludges, at otherwise dry material operations.

5. General reservations were expressed for the need to obtain approvals for operations as waste management facilities, especially for organic materials which are biologically active, and may generate odours.

6. For gypsum board manufacturers, the major issues were the high degree of industry competition; an industry imposed limit of 2.0% organic fibre content (to control the quality of recycled gypsum); the abundance of recycled gypsum; and, anticipated large quantities of by-product gypsum from flue gas desulfurization processes at Ontario Hydro facilities. Provided that formulation and performance information is available, prospects for using paper sludges in gypsum board manufacture could improve.

It is difficult to fathom market prospects for material recovery and recycling, ceramics applications, bioconversion for fuel or food products and other applications identified previously, because the base of information beyond laboratory assessment is limited.

Individual mills and companies are likely assessing various sludge management options. However, these pursuits are internal and not subject to disclosure. Substantial commitments are required to determine the practical and technical feasibility for using paper industry sludges in commercial product applications. Most importantly, there have to be established linkages between the pulp and paper industry, potential product manufacturers and markets to ensure that commercially successful uses for paper sludges are realized.

Market prospects for using secondary-only sludges have not been examined. However, there may be prospects with respect to direct land application in agriculture, forestry and land reclamation, as feedstocks in composts, and perhaps the production of organic/agricultural products as fertilizers for general agriculture, horticulture and silviculture. Due to the pending addition of secondary treatment systems, especially at northern mills, there is a significant need to examine, and, where possible, define and develop appropriate uses, and markets for secondary mill sludges.

11. DISCUSSION AND CONCLUDING COMMENTS

The pulp and paper industry generates large quantities of sludge which constitute a significant management problem. Previous sections of this report identified a number of options for sludge management other than by landfill disposal, incineration and land application. Each of the mills in Ontario generates sludges which have variable and, often unique, qualities. Due to the unique properties of individual mill processes, potential uses for paper industry sludge need to be examined on a mill-by-mill basis.

Currently, most of the mills in Ontario possess primary treatment only. Depending on manufacturing processes, and based on available literature, alternative uses for these sludges can be defined. However, it is expected that most mills will have operational secondary treatment systems in 1995-1996, a factor that will result in higher sludge generation rates, and changes in sludge composition. Because few of the added secondary systems are operational at this time, it is difficult to predict the compositional properties of combined primary and secondary sludges that will be produced.

Mills which currently incinerate primary sludges for fuel value face a dilemma. Secondary sludges are difficult to dewater and handle alone, without the addition of expensive polymers. Diversion of primary sludge to enable dewatering of secondary sludge will reduce the volume of material available for energy recovery, and, therefore, result in added costs for fuel replacement, or processes which allow the incineration of combined primary and secondary sludge.

There is a real need to address options for handling and utilizing secondary-only sludges. Previously noted citations (Aldin, 1977; Frederick et al, 1981) described the processing of secondary sludges in kraft systems, and may represent a viable option. These approaches would not be appropriate for sludges derived from groundwood and other mechanical pulping processes. Prospects for handling secondary sludges in sulfite operations have not been explicitly defined.

High-ash primary sludges from fine paper and deinking operations have received considerable attention with respect to fibre and filler recovery, use in cementitious materials or products, and composites. High-fibre, low-ash content sludges from some chemical pulping, groundwood and other mechanical processes would be candidates for fibre recovery and use in fibre filled composites. Material recovery and uses of deinked secondary fibre sludges have been examined for relatively clean high-ash materials. Few data are available relative to the recovery of materials or use of sludges derived from newsprint and other products. Newsprint is rich in fibre and low in clay fillers. However, the inks in recycled newspaper impart a dark coloration to sludge, and, due to difficulties in removing inks, poor quality pulp substitute may be obtained. Research is needed to determine the feasibility of recovering fibre and removing inks from newsprint and other paper product sludges.

The recovery of fibres and fillers from paper industry sludges represents an attractive option, because these components could be reused directly in paper making, or provide market pulp and filler substitutes for use at other mills. Further development and assessment of fractionation methods, technologies and feasibility warrant further attention. Assessments of fibre and filler recovery from technical perspectives need to be combined with rigorous economic analysis to define practical feasibility of this option, on a mill-by-mill basis.

Use of paper industry sludges in building products, and, especially, cementitious composites, ceramics and related materials, represents a potentially significant prospect. In this regard, whole sludge requiring limited additional treatment can be used directly in this group of building products. The potential constraints include the proximity of manufacturing facilities and market conditions, locally and regionally, relative to individual mills. Also, it remains to be defined whether or not the incorporation of secondary sludge solids in building products would compromise the stability and performance of materials on a long-term basis.

The addition of sludges to conventional materials for the production of fibre board and related composites, thermoplastic composites could be viable. Some situations could allow for the use of fine fibre and ash components in some sludges as extenders of filler in the manufacture of adhesives for particle board and plywood or glue-lam wood products. The recovery of lignosulfonates from sulfite liquors, and natural tannins from tree bark could provide a source of phenol substitutes in phenol-formaldehyde resins used in waferboard and particle board production. Fine fibre and clays in paper sludges would be used as extenders in the resin formulations. This potential application has received very limited attention.

Prospects for the production of ethanol and other fermentation products from paper sludge are interesting. However, none of these applications has been tested at pilot- or full-scale to allow for assessment of feasibility. Commercial ethanol production in Ontario has been limited, and primarily based on corn as a feedstock. It is prudent to note that ethanol production from paper mill sludge has been essentially limited to primary sludge, due to the abundance of cellulosic matter. It has not been explicitly indicated that combined primary and secondary or secondary-only sludges could be used as a source of ethanol or other fermentation products.

Regardless of the prospective sludge uses in manufactured products, there is a substantial need for larger-scale product assessment with respect to sludge additions, formulations, and product development that would enable long-term product performance assessment under conditions that would reflect full-scale conditions. Marketing products containing sludges is difficult, and could be made easier if product samples and performance data were available.

12. RECOMMENDATIONS

Based on available technical information, a number of recommendations have been developed for future research and development activities on manufactured product or other commercial uses of paper industry sludges. This report has identified a multitude of potential uses for paper sludges, all of which have technical merit. Due to the breadth of prospective sludge uses, and limited available resources, it is necessary to focus on key needs, and those options which have the best prospects for commercialization. The principal recommendations arising from this study are itemized as follows:

1. There are good prospects for recovering usable fibre and fillers from paper sludges in paper making, and, therefore, this area warrants further assessment for sludges from a variety of different mills and product lines. Wet air oxidation processes have been extensively examined in this regard, but have not been adopted widely due to costs. In light of current economic and environmental circumstances, it is prudent to revisit potential uses for this technology as well as cleaning and screening technologies which have resulted in commercial scale recoveries of fibre and filler from some sludges.

2. Pending the experimental results and recommendations resulting from the study by Dr. H. Tran and colleagues at the University of Toronto, the use of paper sludges in cementitious product applications warrants considerable attention.

3. Commercial uses of combined primary and secondary paper sludges, including recycling and building products for example, need to be supported by rigorous development of product formulations, and product testing. Concerns expressed for the durability, stability and/or performance of products containing sludge under short- and long-term conditions warrant specific attention. Although initial bench-scale testing is required for many of the prospective applications, larger-scale pilot studies are required to establish the practical and technical feasibility of each sludge use option.

4. Apart from the use of paper sludges in cementitious materials, other building product applications, such as fibre composites, are attractive. Sludge could be utilized as a fibrous feedstock, or as an extender/filler in resins used to manufacture particle board, waferboard and glue-lam lumber products. This potential application for paper sludges has received limited attention.

5. A rigorous economic and market assessment of sludge use prospects needs to be completed to determine current conditions and to focus technical assessments based on interests and issues associated with individual mills. Also, there is a substantial need to define viable markets for sludge uses relative to local (mill) and regional conditions.

6. In view of "green industry" developments within the last five years, and, specifically, the Build Green program, efforts should focus on linkages with the pulp and paper industry to define, and, where possible, develop commercial enterprises that can use paper sludges.

7. The vast majority of prospective paper sludge uses have been based on primary or combined primary-secondary sludge materials which are generally rich in usable fibre and/or fillers. There is a real need to define prospects and opportunities for using secondary-only sludges, especially to alleviate the potentially costly diversion of primary sludge solids from energy recovery systems at some northern mills.

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APPENDIX 1 Pulp and Paper Production Processes

(29 pages)

This section provides details on the major manufacturing processes associated with integrated pulp and paper mills. Non-integrated paper mills rely on market pulps which have been prepared elsewhere. In these cases, the principal production processes are limited to pulp/stock preparation and paper making. The technical content presented was derived from Sittig (1977), and Smook (1982).

Table A-1 presents a summary of effluent sources and composition relative to the major manufacturing unit processes described supsequently.

Debarking Operations

Log debarking is essential to ensure that pulp is free of bark and dirt. Whole log pulping (including bark) can be accomplished in kraft processes. Bark is an undesirable contaminant relative to sulfite and mechanical operations. The principal methods of debarking logs are mechanical and hydraulic. Figure A-1 shows a generalized process diagram for wet debarking.

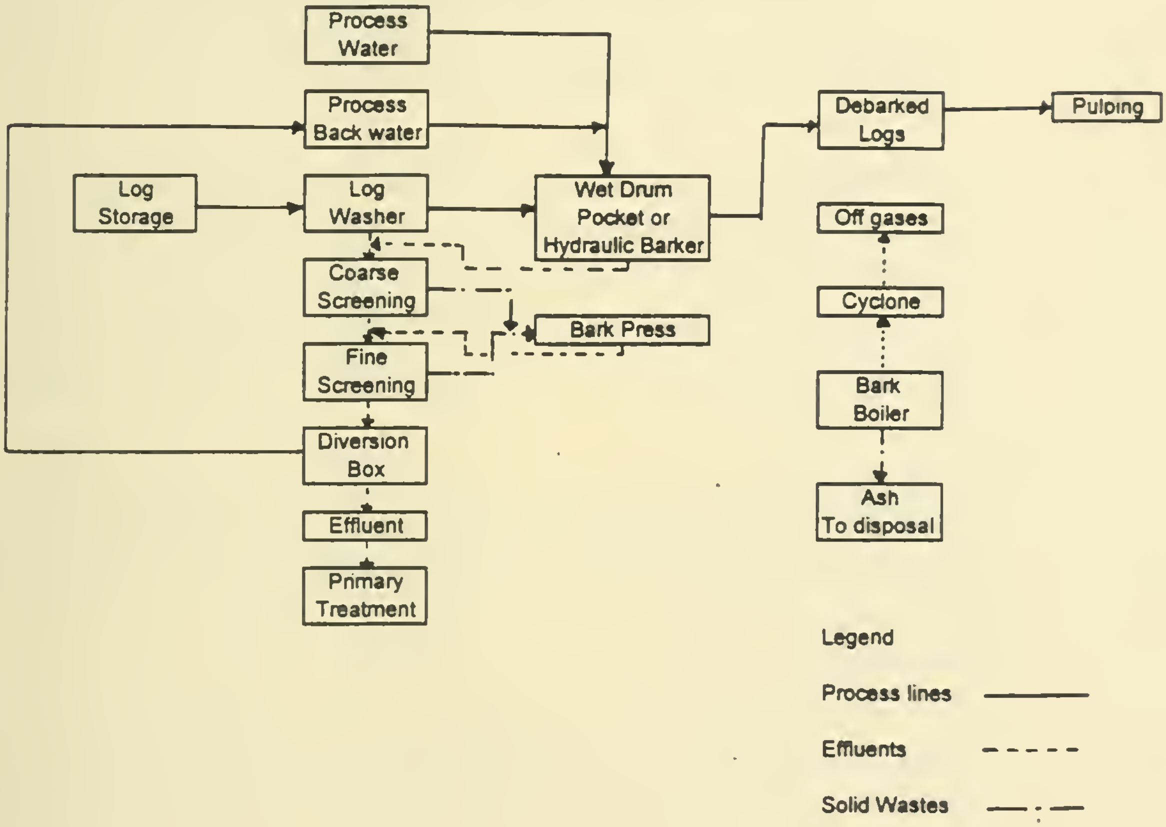
Mechanical debarking is accomplished in barking drums due to the rotating action of the drum and friction between logs in the drum. Slots along the length of the drum enable the removal and collection of bark. In wet debarkers, water is added near the entrance of the drum to loosen bark. Bark and water are removed through slots in the lower portion of the wet drum.

Dry debarking has the advantage of generating bark solids which can be burned without further processing, and also eliminates the effluents requiring treatment. In contrast, wet debarking yields effluents requiring treatment, and wet solids which require dewatering and pressing before

TABLE A-1: Effluent sources from various manufacturing processes

Unit Process	Accessory Processes	Effluent Composition
Debarking		
Dry		none
Wet		bark, wood, sand grit and dirt
Chipper		none
Chip washing		fine fibre, dirt and grit
Groundwood pulping	pulp washing screening and cleaning reject refining	fine wood fibre, dirt and grit
Thermomechanical pulping	pulp washing screening and cleaning reject refining	fine wood fibre, dirt and grit
Kraft pulping	pulp (brown stock) washing, screening and cleaning reject refining	fine fibres dissolved organic matter
Sulfite pulping	pulp washing, screening and cleaning reject refining	fine and long fibres, dissolved organic matter
Semi-chemical pulping	pulp washing, screening and cleaning	fibre and dissolved organic matter (small quantities due to process closure
Deinking	pulping, pulp washing screening and cleaning	fine and some long fibres, clay fillers and coatings, ink, grit, dirt and other solids
Pulp bleaching	washing and cleaning	fibre and dissolved organic matter
Paper machine		fibre, fillers and coatings and other solids

FIGURE A-1 : GENERALIZED PROCESS DIAGRAM FOR WET BARKING PROCESSES



burning or disposal. Soluble matter contained in bark, including resins, tannins and other constituents are difficult to treat.

Screening of wash water from wet debarking will remove coarse solids including bark, wood, grit and dirt. Screened effluents will include bark and wood fines, and various inorganic solid components which would be sewered to the primary treatment plant.

Hydraulic (jet) barkers are most common on the West Coast, where they are used to process large diameter logs. These systems operate by directing high pressure jets of water to remove bark from logs. Although bark removal is efficient, with minimal wood losses, hydraulic barking systems have high energy requirements, and yield effluents which are difficult to treat.

After debarking, logs may be stored for groundwood pulping or reduced to chips for chemical and thermomechanical pulping.

Wet woodroom systems may utilize 20,000-150,000 L/min of water for cleaning and/or washing, of which up to 10,000 L of effluent may be generated for treatment. Centrifuge cleaners can reduce effluent volume to 1,000 L. Effluents can yield about 40 kg of suspended solids per tonne (oven dry) of wood. This concentration may be reduced to 3.0 kg/T if woodroom effluent is clarified.

Due to difficulties in treating effluents from debarking can be difficult, many operations have shifted to completely dry woodroom processes.

Chipping

Debarked logs are reduced to chips for subsequent chemical and thermomechanical pulping. Logs are reduced to chips of about 12-18 mm. Coarse rejects are removed to a reject refiner for reprocessing. Fines from chipping operations must be removed to prevent clogging of liquor circulation screens, and pore plugging of pores between chips which restrict the circulation of pulping liquor in digesters. Air cleaning, mechanical screening and washing may be employed to remove fines. Chip washing processes represent the principal source of effluents and suspended solids requiring further treatment.

Pulping Processes

Pulping processes generally involve the conversion of the wood chips and logs into pulp for paper making and include the wood pulping, pulp bleaching and accessory unit processes encountered in "pulp mills". In this report, reference to pulping processes is limited to the wood to pulp conversion process.

Wood consists of about 45% cellulosic fibre, 20-30% lignin, 25% hemicellulose, 5% extractables, and <5% ash (inorganic constituents). The basic objective of pulping is to loosen and separate individual wood fibres to enable paper making, and is accomplished by mechanical and/or chemical methods. Mechanical pulping processes yield wood fibre which retains most of the lignin and hemicellulose components. In contrast, chemical pulping results in the solubilization and removal of non-fibrous materials. Differences in pulping processes versus pulp yield are variable as shown in Table A-2. The highest yields are obtained from mechanical pulping, whereas low yields are obtained from chemical pulping (kraft and sulfite). Not shown in Table A-2 are the yields associated with deinking

TABLE A-2: TYPICAL PULP YIELDS

Unbleached kraft	50-55 %
Bleaqched kraft	43-48 %
Dissolving sulfite	33-40 %
Low yield sulfite	46-55 %
Medium yield sulfite	55-65 %
High yield sulfite	65-80 %
Chemi-thermomechanical (CTMP)	80-90 %
Thermomechanical (TMP)	91-95 %
Stone groundwood	94-96 %
Deinked newsprint	85%
Deinked fine/ledger	75%

Note: Yields >90 % are estimates only due to variations in measurement methods.

and secondary fibre processing which may yield losses as high as 35%, and consisting of small fibres, fillers, coatings, inks and other solids (Bruce, 1994).

Pulp yield provides a relative indication of effluent quality and index of the sludge output from effluent treatment, especially for systems where the recovery of pulping chemicals and soluble matter is not achieved. In general, higher pulp yields will result in lower waste and effluent strength in terms of suspended solids and soluble organic matter. Mechanical pulping processes yield effluents containing fine wood fibres, whereas the chemical pulping processes (kraft and sulfite) yield effluents containing higher proportions of soluble matter.

Mechanical Pulping

Groundwood and thermomechanical processes are the most prominent forms of mechanical pulping employed at Ontario mills.

Groundwood process. The most common and oldest form of mechanical pulping is referred to as stone groundwood. In this process, debarked logs are forced against a revolving grindstone to tear and separate the wood fibres. Spruce, balsam fir, jack pine, poplar and assorted hardwoods are commonly used. Spruce, especially black spruce yields bright and strong groundwood pulp, while inferior quality pulp is produced from jack pine due to high pitch content and darker colour. Poplar yields low strength pulp, but with good ink absorbency. Water is applied during grinding to cool and lubricate the stone, and also to remove the fibres.

Groundwood pulp can contain slivers or shives up to 1.0 m in length. These coarse fragments must be removed by screening before further processing. Other coarse fibres and fibre conglomerates, captured by screening, are sent for re-refining. Fine fibres are retained in groundwood effluent, and constitute the major solid fraction entering effluent treatment systems.

Figure A-2 presents a generalized process diagram for a groundwood pulping system. Included in Figure A-2 are the principal effluent sources, which are associated with log preparation/grinding, screening, washing and refining.

Refiner mechanical pulp. Refiner mechanical pulping (RMP), also referred to as refiner groundwood, was introduced in the late 1950s. The RMP process involves the reduction of wood chips to pulp using single or double disc refiners followed by centrifugation for fibre classification. For some applications, chip preparation is required, e.g. washing to remove sand, grit and dirt. Water and chemicals are added to establish the appropriate pulp consistency.

A significant advantage of the RMP process, relative to stone groundwood pulping, is the ability to use chips and cutoffs from sawmill operations, while stone groundwood process depend on solid logs. Disc refiners also enable the use of sawdust and shavings. High energy requirements for RMP processes have resulted in replacement by thermomechanical pulping.

Thermomechanical process. Most of the mechanical pulping capacity installed since 1973 has been based on the thermomechanical process (TMP). Figure A-3 shows a generalized process diagram for the TMP process. The principal difference between RMP and TMP processes is the refining process. RMP systems rely on pulping and refining under atmospheric pressure, while TMP processes rely on at least one stage of

FIGURE A-2 : GROUNDWOOD PULPING PROCESS DIAGRAM

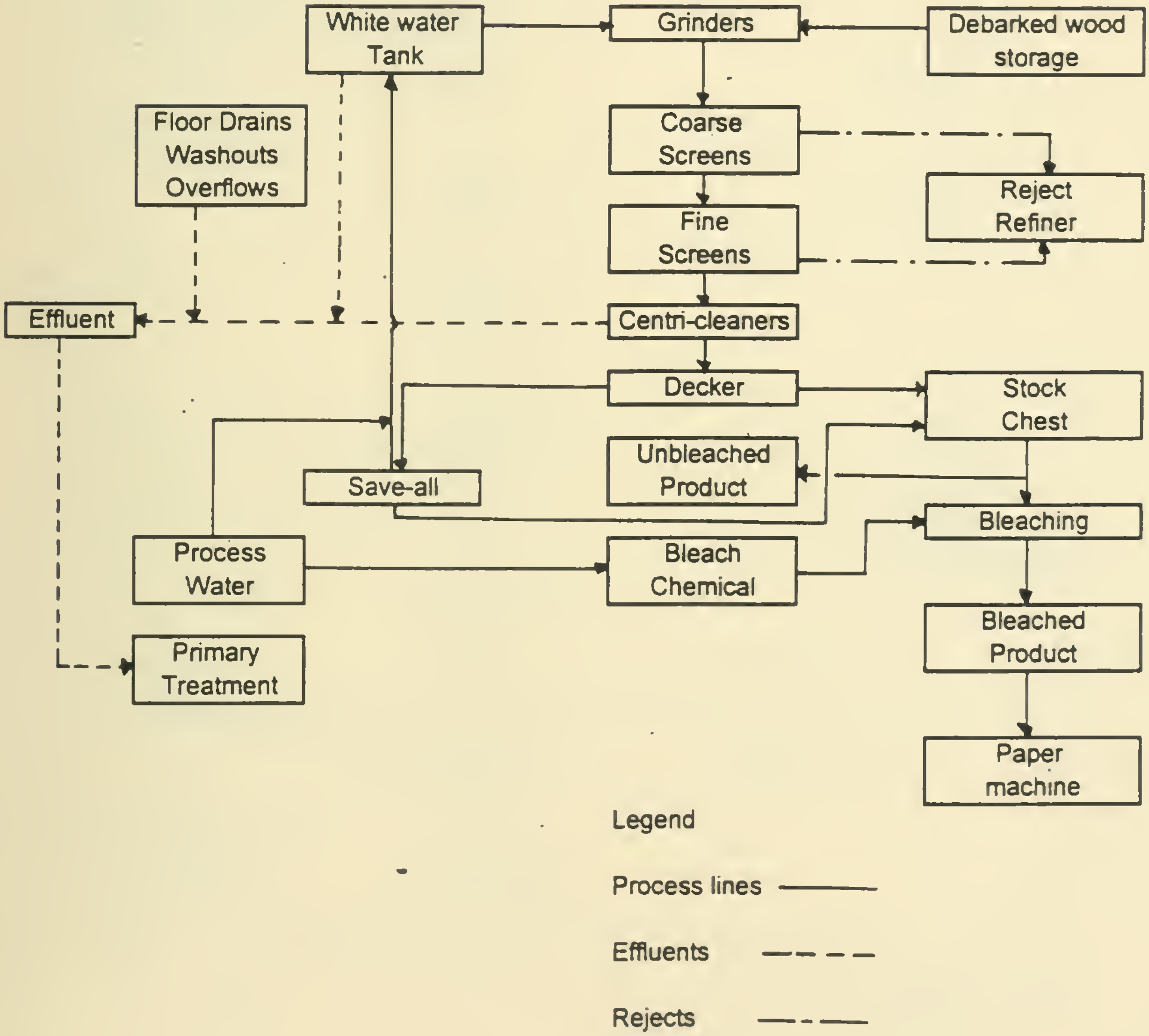
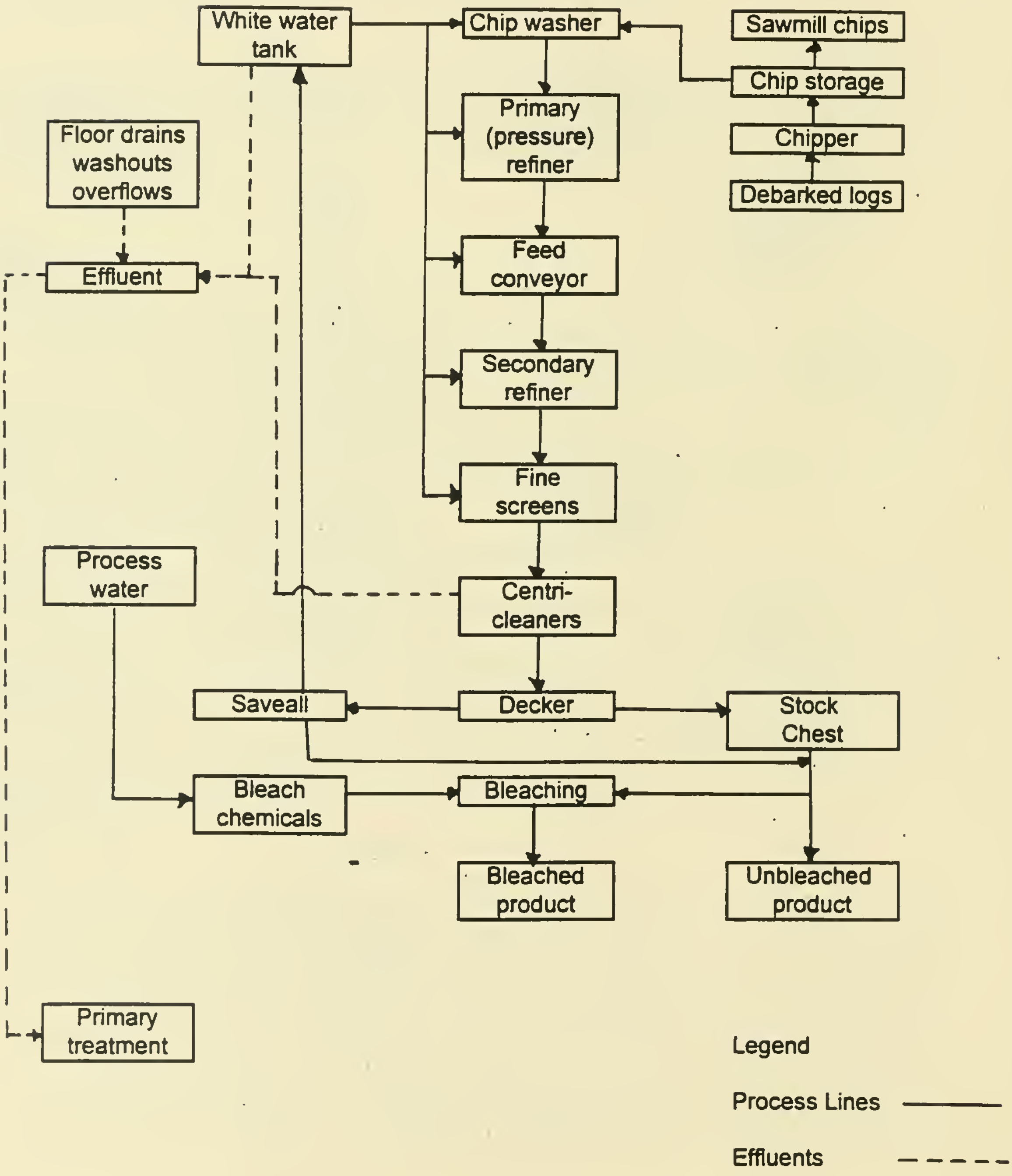


FIGURE A-3: THERMOMECHANICAL PULPING PROCESS DIAGRAM



pressurized treatment. In the TMP process, wood chips are softened by pressurized steam, without chemicals, and subsequently defibred in a pressurized disc refiner. Raw pulp is subject to further refining (second stage refiner) before screening and cleaning. Although pulp yields are somewhat lower than for groundwood (Table A-2), strength and paper making properties are superior.

Washing of chips before refining is essential to minimize the entry of sand, grit, dirt and metal fragments into the process. Heavy solids are removed by gravity and size. Most of the water used in the cleaning process is recycled, however, a portion of the effluent is wasted to the treatment plant.

Recent variations of the TMP process use small quantities of chemicals during pulping, and are thus, referred to as chemi-thermomechanical processes (CTMP). For instance, weak solutions of sodium sulfite are added to the steaming vessel to soften the wood chips. This improves pulp quality, but results in lower yields, due to the partial solubilization and removal of lignin and other wood constituents.

The principal effluent sources in the TMP process include tertiary cleaners and rejects from chip washing.

Chemical Pulping

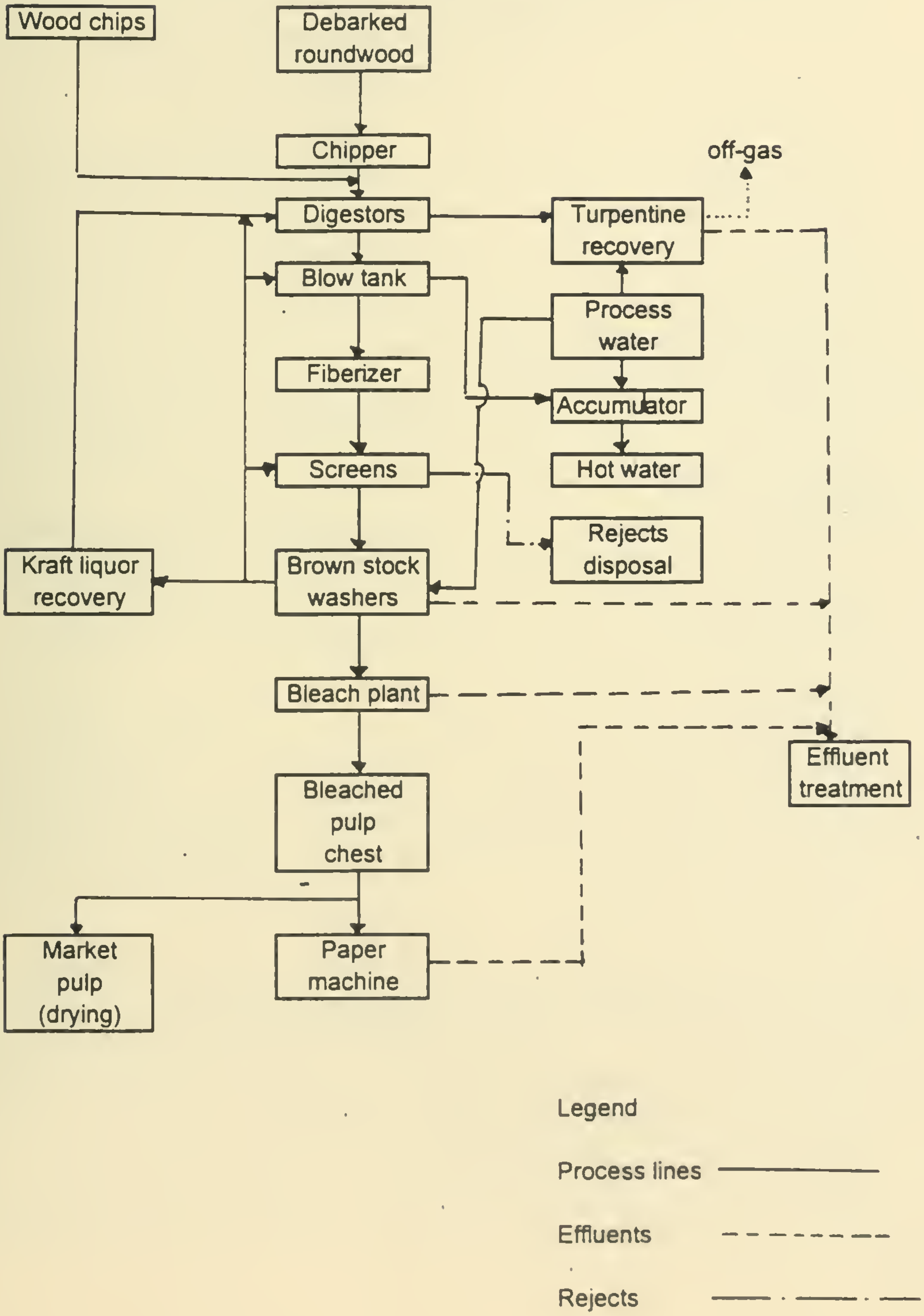
Chemical pulping processes are dominant at integrated pulp and paper mills in Ontario. The two prominent chemical pulping processes are sulfite (acid to low pH) and kraft (alkaline). In chemical pulping, fibre separation and preparation is accomplished by chemical energy. Pulp yield, as shown in Table A-2, is lower for sulfite and kraft processes when compared with mechanical pulping. The lower yields associated with chemical pulping are due to the solubilization and removal of non-fibrous lignin and hemicellulose components in the wood chips. Woods containing high percentages of resins and fats are readily pulped by the kraft process. In contrast, sulfite systems work the best for low resin woods such as spruce.

- **Kraft pulping**

Figure A-4 shows a generalized process diagram for kraft pulping operations. The kraft process has become the dominant chemical pulping process. The recovery of valuable pulping chemicals, versatility, and flexibility relative to various wood species offer significant advantages relative to sulfite pulping. Wood extractables from some species such as pine lead to problems with pitch in sulfite operations, but are readily dissolved or dispersed in alkaline kraft liquors. Also, certain carbohydrates degrade in an acidic medium (sulfite), but are generally stable in alkaline kraft processes. The relative rapidity of the cooking process and high pulp strength are further advantages of the kraft process. The principal disadvantage is that residual lignins in kraft pulp impart a dark colour. Unbleached kraft is suitable for paper bags, packaging and other products. Because a substantial fraction of lignin remains in kraft pulp, additional cooking leads to the degradation of carbohydrate fractions. For writing and fine papers where brightness is a requirement, pulp bleaching is required to further delignify the feedstock. Multistage bleaching is required to brighten kraft pulps for these uses. In contrast, the higher levels of brightness encountered with sulfite pulps require fewer bleaching stages.

The kraft process involves the cooking of wood chips in an alkaline solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). Due to the common use of sodium sulfate in the chemical make-up of the pulping

FIGURE A-4 : KRAFT PULPING PROCESS DIAGRAM



liquor, kraft pulping is also referred to as the sulfate process (API - Table 1). Alkaline attack of the lignin in the wood chips yields salts which are soluble in the cooking liquor and subsequently removed. Due to chemical attack, the fibre yield amounts to 40-50% relative to the initial feestock.

The cooking process can be either batch or continuous, with the latter being adopted at most kraft mills. In continuous processes, wood chips are initially steamed before entering the digester, to remove condensable gases and volatile components such as terpenes. Subsequently, the chips are fed to the digester, which is charged with the cooking liquor (white liquor) at a controlled temperature. This enables impregnation of the chips by the liquor. After a designated period for impregnation, the temperature is increased by indirect heating of the circulating liquor for a period of about one hour. The pulp is then quenched with wash liquor. Diffusion washing is undertaken in the lower region of the digester, and results in the removal of considerable quantities of the pulping liquor. This washing process ensures suitable blow conditions with minimal mechanical damage to the fibres.

Batch cooking involves the addition of the chips and cooking liquor to the digester, which is then sealed. Cooking pressures and temperatures are raised to predetermined levels, and for a prescribed period. After digestion, the pulp is blown hot to the blow tank and diluted with black liquor before washing.

Pulp in the blow tank is typically mixed with black liquor, and must be separated from it. The process of separating the pulp from black liquor is referred to as brown stock washing. Virtually all of the material washed from the pulp will form part of the effluent streams. The dissolved organics are toxic to fish and resistant to treatment. Efficient washing transfers the organic materials and chemicals from the effluent to recovery processes.

Chemical recovery processes associated with kraft operations do not yield effluents. In this regard, black liquor and associated effluents, containing appreciable quantities of organic matter and pulping chemicals are processed to destroy organic fractions and recover the inorganic chemicals for use in the production of fresh pulping liquor.

- **Sulfite pulping**

Figure A-5 presents a simplified process diagram for sulfite pulping. In the sulfite process, wood chips, primarily from softwoods (spruce and fir) are pulped in a mixture of sulfurous acid (H_2SO_3) and bisulfite (HSO_3) to solubilize and remove lignin. The chemical bases for bisulfite include ionic forms of Ca^{2+}, Mg^{2+}, Na^+ and NH^{4+}. Na and Mg based sulfite pulping processes are represented in Ontario. As shown in Table A-2, pulp yields are higher for sulfite relative to kraft, due to the incomplete solubilization and removal of non-fibrous matter in sulfite pulping.

Although sulfite pulping is often referred to as "acid sulfite", the pH of pulping liquors varies from 1-2 for liquors containing excess H_2SO_3, to 3-5 for HSO_3 processes.

Sulfite pulping require clean chips, and therefore washing is essential prior to pulping.

The cooking or pulping liquor is typically prepared by burning sulfur to produce SO_2 gas, and subsequent absorption of SO_2 in an alkaline base solution. Raw cooking acid after SO_2 absorption is a mixture of free SO_2 and combined SO_2 in desired proportions. The raw acid is fortified with SO_2 relief gases under both low and high pressures.

Cooking operations are usually accomplished in a corrosion resistant pressure vessel or digester. The digester is first filled with chips, then capped. Hot acid is added from an accumulator, to nearly fill the vessel. Heating of the charged vessel follows a prescribed schedule by recirculating the liquor through a heat exchanger. Pressure in the gas pocket at the top of the digester is allowed to increase to a predetermined level, and then SO_2 is bled off to be absorbed in the accumulator.

As the temperature and pressure increase, the hot acid is rapidly absorbed by the chips. The chips are cooked for six to eight hours to avoid lignin polycondensation reactions. Near the end of the cooking process, the pressure is gradually reduced, and the chips are blown into a blow tank or blow pit. Water is applied to the chips to remove residual pulping liquor. The resultant pulp is then screened and cleaned. Spent pulping liquor is then sent to recovery which eliminates the organic chemicals and enables recovery of pulping chemicals.

Sulfite pulps are generally lighter in color and require less extensive bleaching when compared with kraft pulps.

Effluent sources in sulfite processes include the pulp washing, screening and decker stages as shown in Figure A-5. Effluent components could include portions of residual liquor, dissolved organic matter and small quantities of fine fibres. Generally the recovered liquor is captured and burned.

- **Semichemical (Neutral sulfite - NSSC) Pulping**

Figure A-6 shows a generalized process diagram for semichemical pulping, typically employed in the production of pulps for container board and corrugating medium.

FIGURE A-5 : SULFITE PULP MILL PROCESS DIAGRAM

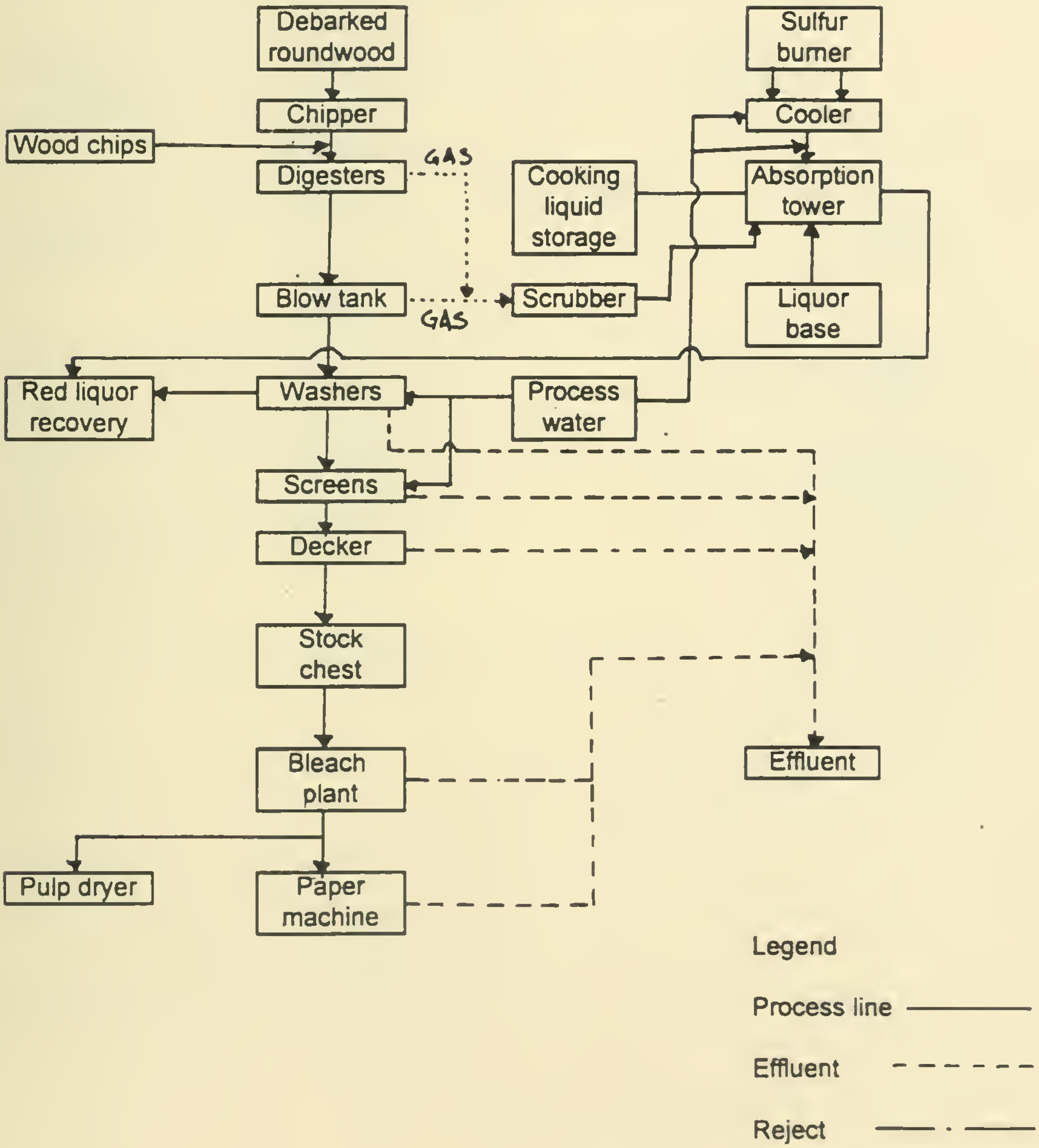
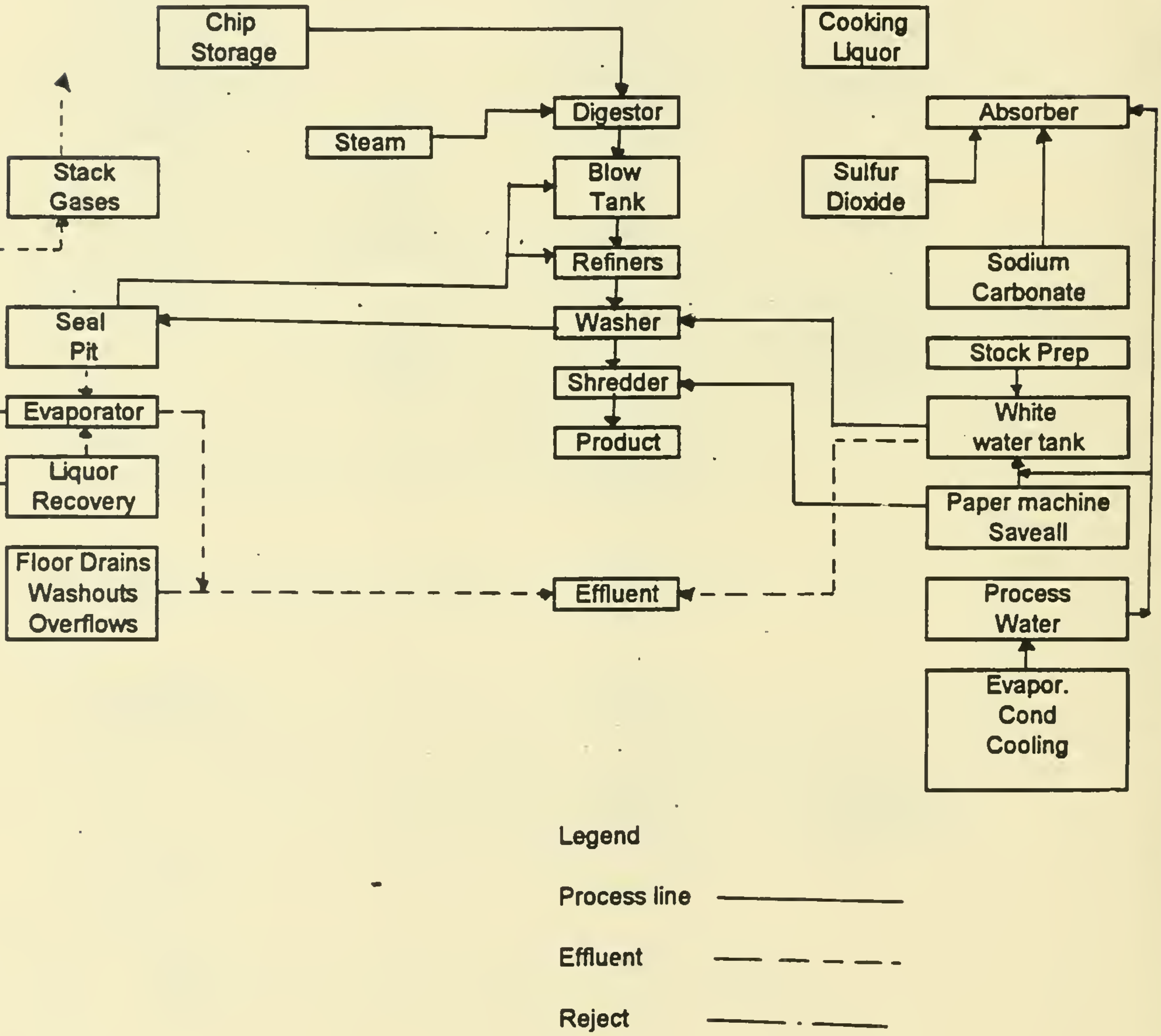


FIGURE A-6 : NEUTRAL SULFITE SEMICHEMICAL PULP PROCESS DIAGRAM



Wood chips are cooked with a sodium carbonate and sodium sulfite liquor to partially remove the lignin in the chips. The NSSC process yields a less aggressive attack on the wood fibres with higher resultant yields than kraft. The process is undertaken in two stages. Wood chips are initially softened by a short cook, in either batch or continuous digesters, then processed in a disc refiner before washing. Pulp wash water and drainings from the blow tank are sent to the boiler for recovery or burning. After washing, the pulp is transferred to an agitated chest where it is diluted with white water to a desired consistency, subsequently fed to secondary refiners and then on to the paper making process.

Spent NSSC liquors and effluents tend to be high strength and cannot be discharged without treatment. Recent developments have led to a high degree of mill process closure, and, hence, the minimization of effluent discharge. Spent NSSC pulping liquors have been utilized for some time as binding agents on unpaved roads.

- **Secondary Fibre Utilization and Deinking**

Secondary fibre includes any fibrous materials that have undergone a manufacturing process and are to be recycled as raw material for another product (Smook, 1982). Strictly speaking, broke from the dry end of the paper machine, finishing room trimmings and repulped rolls could be considered as secondary fibre sources. However, in practice, internal recycling of fibre is not included in the broad group of secondary fibre. In keeping with the definition of Smook (1982), secondary fibre is derived from waste paper and paper products - post-consumer residuals. Waste paper recycling has been most significant in the production of paperboard products and, to a lesser degree, newsprint and building grade papers for several decades (Sittig, 1977).

Although any paper can, in theory, serve as a source of secondary fibre, the quality of the secondary fibre source is dependent on the waste material attributes. Good quality feedstocks depend on sorting and classification to ensure consistency of fibre quality. Classified waste paper yields the highest prices. In contrast, mixed and unclassified waste paper commands lower prices due to variable consistency, and potentially high degrees of contamination by plastics, glues, metals, glass, synthetic coatings, sand, grit and dirt. Considerable costs can be incurred for the processing of low quality or unclassified waste paper, and, due to the difficulty of removing some of the contaminants, imperfections and poor paper qualities may result. The best grades of waste paper - envelope trimmings, business products and uniform newsprint - yield the highest secondary fibre pulp qualities. These materials can be used as substitutes for virgin fibre pulp in a variety of products (Smook, 1982).

Interestingly, the escalating demand for high quality waste paper for deinking and secondary fibre use has captured most of the available supplies, and has contributed to higher prices for secondary fibre pulp substitutes. Reduced supplies of good quality waste paper have also forced processing of inferior grades with resultant higher processing costs, and potentially higher waste output. Lower grade papers must be cleaned up in the secondary fibre pulping system.

It was generally accepted that 50% is the practical maximum recycle rate (Smook, 1982), although a number of mills, including two in Ontario, produce paper exclusively from deinked secondary fibre pulp. Significant losses of fibre and reductions in strength occur with each recycle step. At the 50% recycle rate, it has been assumed that up to one-half of the waste paper matrix has undergone at least one recycle sequence. Effects of multiple fibre recycling are evident from progressive reductions in sheet strength and bonding potential or strength. Data presented by Smook (1982) showed significant reductions in both strength parameters associated with multiple newsprint recycling. Dramatic losses in bonding strength have been attributed to loss of fibre flexibility and water permeability associated with drying, when compared virgin fibre. Cumulative losses of hemicellulose from fibre surfaces also contribute to reduced bonding strength.

The heart of the secondary fibre recovery process is the continuous pulper with ragger and junker. Centrifugal action of the continuous pulper literally throws the junk and heavy solids to the outside of the pulper where it can be captured and removed. It is prudent to emphasize that not all of the junk or contaminants can be removed physically or chemically, especially lightweight materials and very fine matter - fibres, clays and inks.

Deinking process. The process diagram for a deinking operation and secondary fibre recovery is shown in Figure A-7. Deinking is essentially a laundering process. Chemicals are added to the pulper to remove inks, and to separate the fibres from fillers, coatings and other components. Light contaminants are not removed at this stage. The combination of chemicals, heat and mechanical energy are used to remove inks. The three major chemical groups added to the process include:

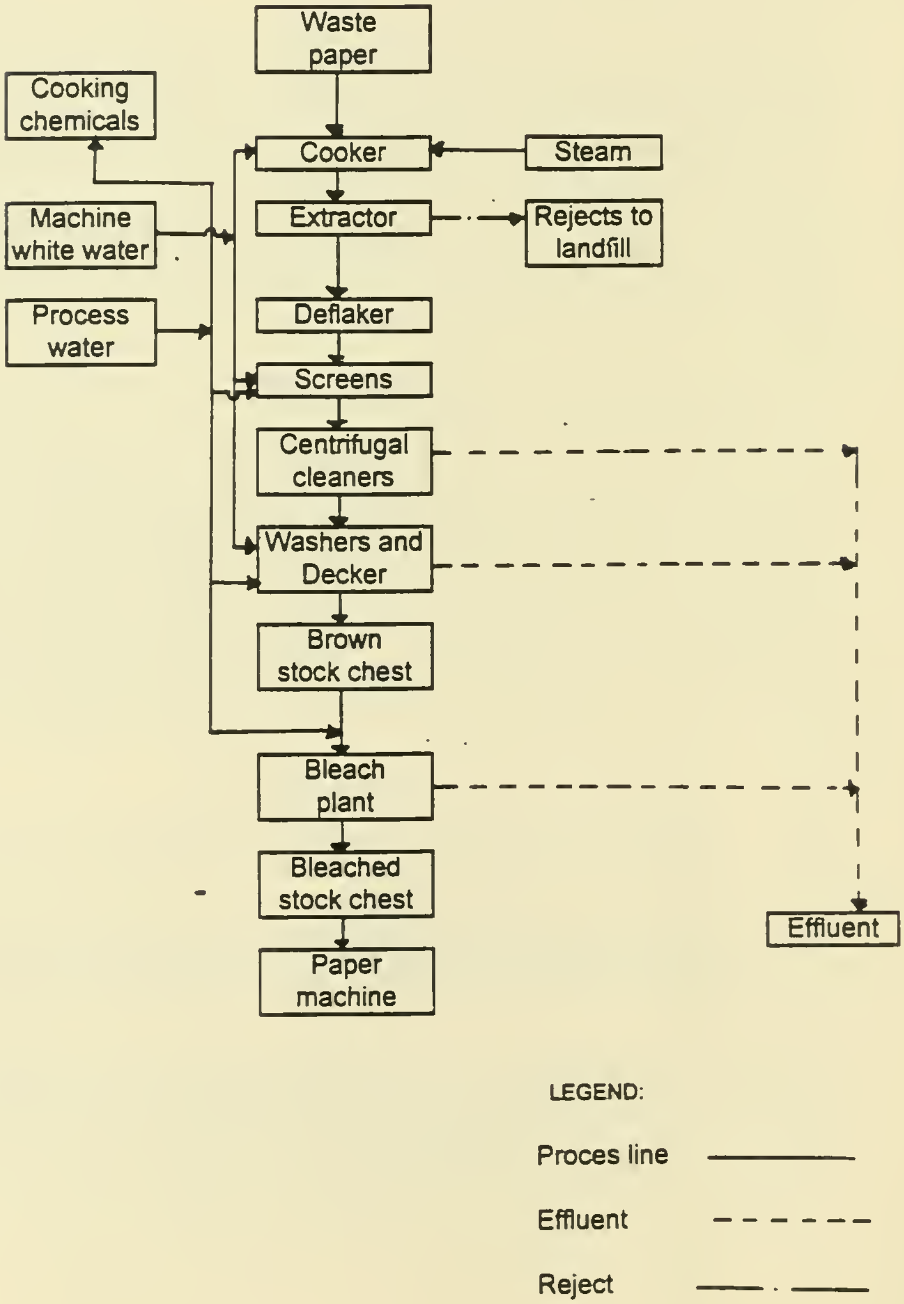
(1) detergents or surfactants to remove ink

(2) dispersants to maintain separation of inks and to prevent redeposition on the fibres

(3) foaming agents which reduce the surface tension of water, and enable the skimming of light materials from the surface.

Two deinking processes are employed and defined as: washing and flotation. Washing operations are the most common, although, flotation systems are being added, at least at new mills.

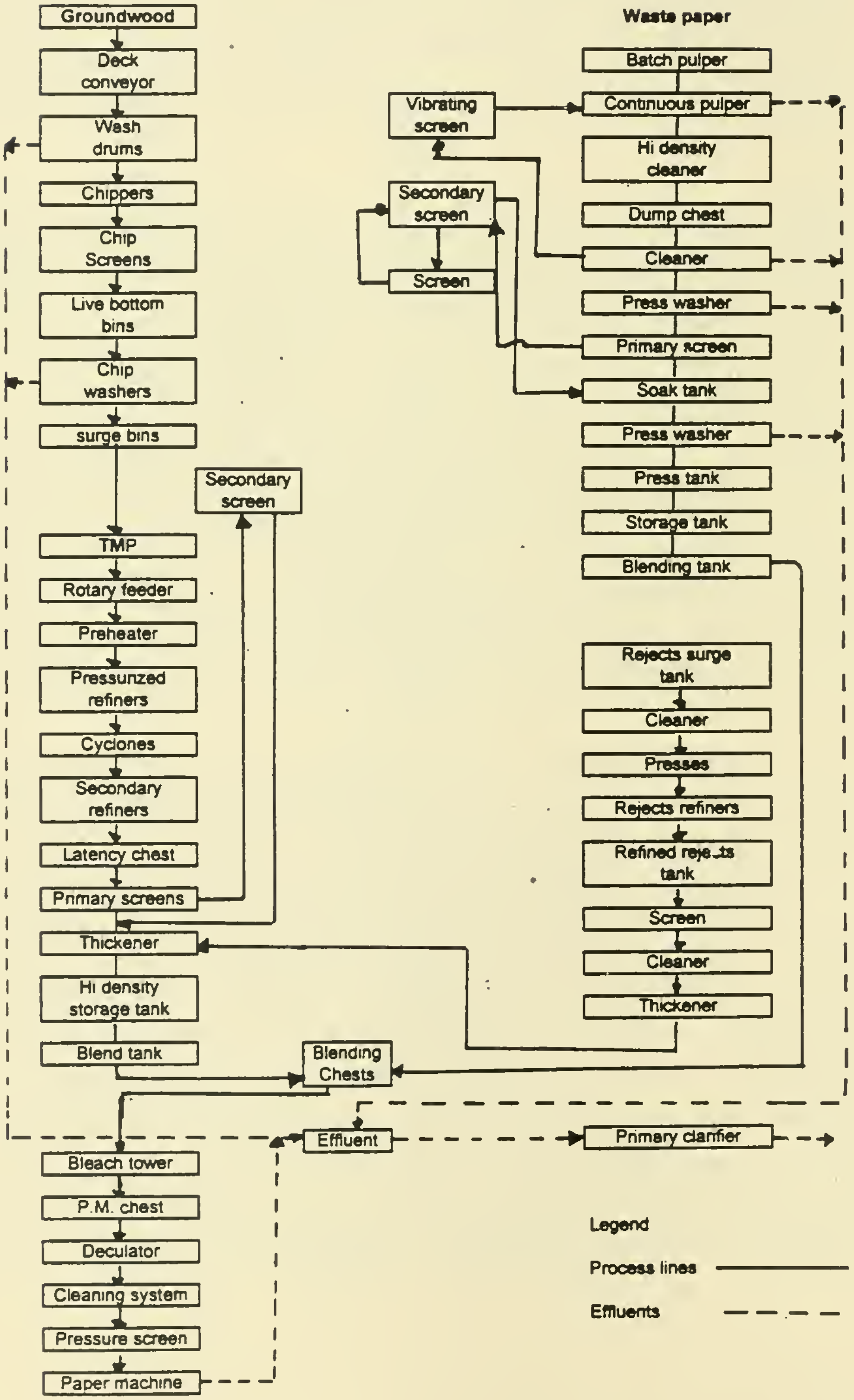
FIGURE A-7 : DEINKING PLANT PROCESS FLOW DIAGRAM



Secondary fibre pulp washing is a multi-stage process. Clarified water is typically used in the last washing stage before the clean pulp is further processed for paper making. Effluent solids are derived from the first and second washing stages and consist of fine fibre, fillers and coatings, inks, dirt, grit and other materials. These effluents are collected and sent to the effluent treatment plant.

Flotation systems are most common in Europe, although newer deinking plants in North America are being set up with these systems. The costs of flotation systems are higher than washing operations. However, there are major advantages. In flotation systems, the pulping and deinking processes occur in the pulper. Chemicals are added to promote separation of inks from fibre, and foaming to remove flocs of ink solids from the surface. Fibre yields are higher with flotation systems relative to washing processes. Because the deinking chemicals are concentrated in the foam or froth, cleaning requirements are lower and effluent treatment is simpler. The main drawback associated with flotation processes is that less of the fillers and fines are removed, which could affect product quality.

As stated previously, there are six established deinking operations in Ontario. Four of the mills combine deinked secondary fibre pulp with virgin fibre pulp to varying degrees. In this regard, the secondary fibre pulp is blended in varying proportions with virgin fibre pulp for further blending, bleaching and preparation before paper making. Figure A-8 presents a generalized process train for combined TMP and deinking operations for newsprint production. As shown, the respective pulping processes are distinct, but the effluents from the entire operation are combined for treatment in one effluent treatment plant. Effluents, and ultimately sludges, from these operations will possess properties which reflect the combined virgin fibre, deinking and secondary fibre processes. Two of the six operations depend exclusively on deinked secondary fibre, FIGURE A-8: PROCESS DIAGRAM FOR COMBINED GROUNDWOOD, TMP AND DEINKING.



and, thus, the process configuration shown in Figure A-7 is appropriate for these cases.

Pulp Bleaching

Bleaching of pulps is required to varying degrees, depending on product types and applications. Groundwood pulps may be sent directly to paper making operations, or bleached. Groundwood pulp bleaching is accomplished by peroxide or hydrosulfite (zinc) , washing and preparation for paper making.

Chemical pulps are typically bleached in multiple stages. Kraft pulp bleaching, using chlorine, chlorine dioxide, hypochlorite and oxygen, is required for various product lines to eliminate the "brown" colour and to enhance brightness. The chemical bleaching agents are used to delignify the pulp in stages. Alkaline extraction and washing are used between bleaching sequences to remove the solubilized lignins. A four-stage bleaching sequence for kraft pulp is shown in Figure A-9. Due to the higher brightness of sulfite pulps, fewer bleaching stages are required when compared with kraft processes, as indicated in Figure A-10. Pulp from sulfite or groundwood that is used in newsprint may require minimal or no bleaching. Paperboard (NSSC) and other products generally require no bleaching.

As shown in Figures A-9 and A-10, a number of stages in the bleaching processes yield effluents which are sewered for treatment. Dissolved solids and fibre would be present in these effluents. Caustic streams or effluents derived from alkaline extraction stages in kraft bleaching processes are often handled separately from other mill effluent streams. The resultant lime sludges are handled/disposed of separately. The

FIGURE A-9 : FOUR-STAGE KRAFT PULP BLEACH PLANT PROCESS FLOW DIAGRAM

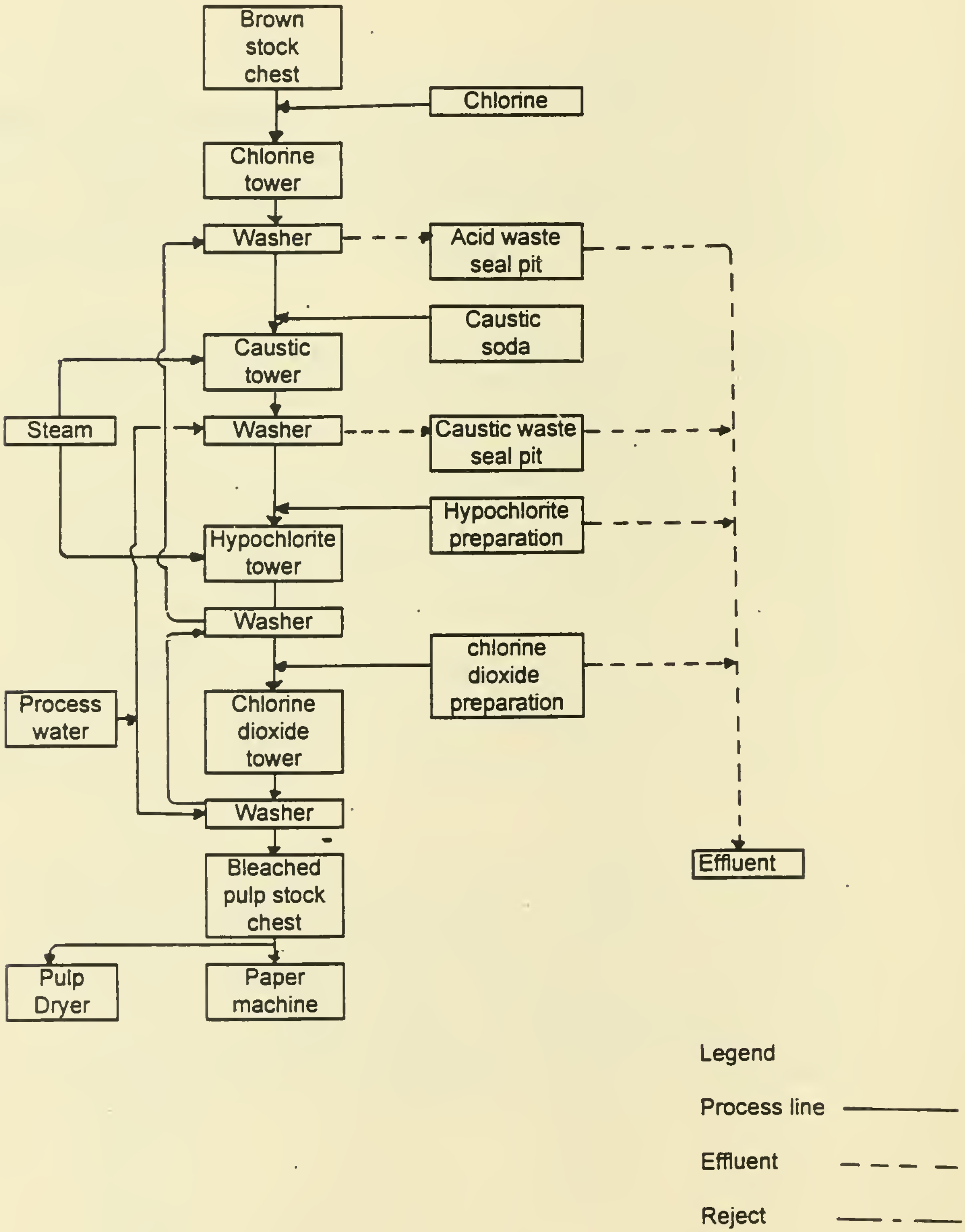
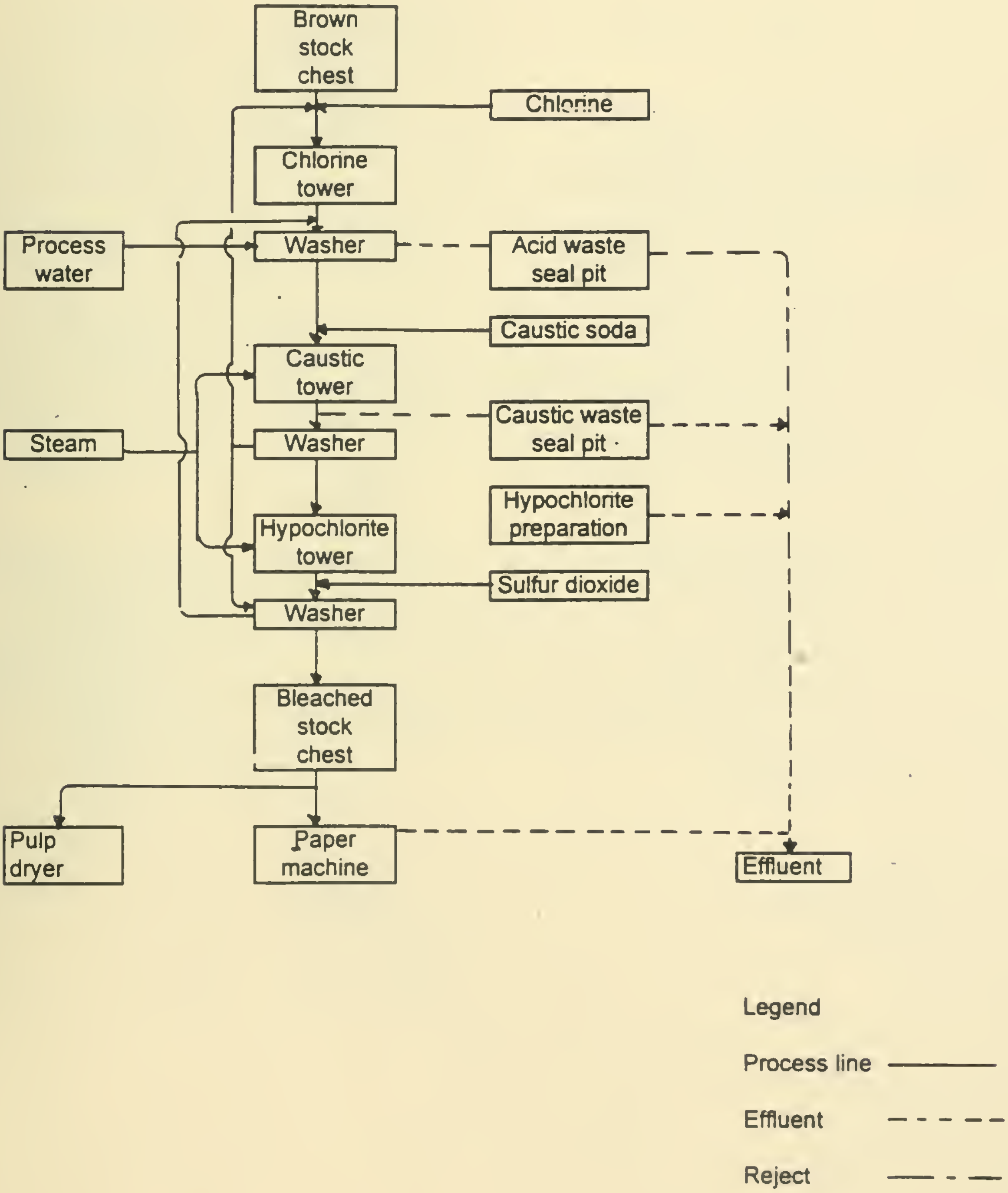


FIGURE A-10 : SULFITE PULP BLEACH PLANT PROCESS FLOW DIAGRAM



qualities of these lime sludges are amenable for use as substitutes for agricultural lime (NCASI, 1984; Thacker, 1986).

Paper Production

Paper and paperboard production is accomplished by forming a matrix of fibres on a web, screen or wire. Pulp is prepared by adding water in the stock chest to achieve the desired consistency, beating the fibres and adding sizing, fillers and other materials. A general paper making process diagram, which is applicable to integrated and non-integrated mills, is shown in Figure A-11 Water is removed from the sheet by pressing between rollers in the paper machine and steam or, in some cases, dry heat. Because of the relatively low consistency of the pulp entering the paper machine, considerable quantities of waste water or effluent are produced.

Data compiled by Sittig (1977) show the varying quantities of additives used in paper making. Depending on the process and product lines varying quantities of rosin, sizing agents, clay (kaolin) fillers and coatings, pigments, talc and other materials may be added. Varying quantities of these additives will appear in the effluents from paper production processes.

FIGURE A-11 : PAPER MANUFACTURING PROCESS FLOW DIAGRAM